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THEORIES OF ORGANIC CHEMISTRY

BY

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Professor in the University of Erlangen

Translated and Enlarged from the Revised Fourth German Edition of 1921

BY

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AND

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PREFACE TO THE AMERICAN EDITION

THE general theory of Organic Chemistry is at present in a state of violent transformation. While the old hypothesis of valency with the accepted division into single valencies on the atoms has not yet by any means been abandoned, it is nevertheless no longer looked upon as a *noli me tangere*. On the contrary, an ever-increasing number of observations would seem to indicate that the division of the original valency force present on the atom is in reality an unequal one and may even vary under different conditions.

This view already discussed by A. Claus in 1881 has received experimental support from facts discovered in the course of investigations on free radicals (Triphenylmethyl, etc.). A more detailed study of the physical properties of organic compounds (such as the relation between color and constitution) has, moreover, served to connect conceptions regarding the inner structure of the molecule with the "Electron Theory of the Constitution of the Atom." For example, observations as to what parts of the molecule are especially influenced by light may be made the basis for discussion in regard to the mechanism of molecular formation in all its phases and may ultimately lead to the discovery of a theory which, based upon the new views in regard to the constitution of the atom, will afford a satisfactory explanation for all physical and chemical phenomena.

American chemists have played a considerable rôle in the newer developments and have contributed many fundamental researches. Unfortunately foreign periodicals in Germany have become such a rarity that it is no longer possible to cover the original literature completely.

I am, therefore, very grateful to Professor Treat B. Johnson for filling in some of these gaps. It is to be hoped that the book will be of use to research chemists as well as to the teaching profession and thus lead to an ever greater perfection of our beautiful science.

F. HENRICH.

ERLANGEN, August, 1920.

TRANSLATOR'S PREFACE

THE foreign text by Ferdinand Henrich, upon which the present volume is based, has long been familiar to students matriculating for the M.S. and Ph.D. degrees in the Graduate School of Yale University. It has served not only as a means of stimulating a greater interest in the literature of organic chemistry, but it has also proved a valuable source and guide for advanced seminar discussions. Since, however, the many problems which it represents are interwoven with the developments of all modern chemical theory it seemed desirable to undertake its translation into English and in this way bring it to the attention of a much larger number of our young readers. The task of doing this successfully has been somewhat complicated by the fact that it has often been necessary to rewrite and even to rearrange completely portions of the material in the original text to render it acceptable to the American reader. Thus, for example, the development of a given conception in the original German frequently involves a suspension of the thought through many pages while involved phases of the subject are considered before the actual objective becomes apparent. This procedure would, it was felt, find little favor in translation since the average American prefers to be enlightened as to the particular object in view before venturing upon a long course of speculative reasoning.

The construction of the English text, therefore, has been a very laborious task, and the writer wishes to emphasize here the fact that the present translation would not have been undertaken without the assistance and cooperation of an efficient co-worker in organic chemistry. It is, therefore, my very pleasant duty to record here my indebtedness to Professor Dorothy A. Hahn of Mount Holyoke College for her able collaboration with me in the translation and construction of the text.

One of the conspicuous weaknesses of our present-day graduate students majoring in chemistry is the lack of what may be called the historic sense. There are so many interesting and practical problems of research being placed before them for solution that their attention

is naturally diverted from the older works and focused chiefly upon present-day achievements. In fact, in the present age the opportunities for great and rapid success are so alluring and the appeal of the present and future is so strong that most of us forget what we owe to the past. And because we take so little time to think of what our past leaders in chemical science have given us, we, too, often in our rush and haste have an exaggerated notion of our own immediate work as compared with that of our forefathers. One of the chief purposes of this translation is to stimulate in our graduate students during their period of research training a desire to follow more closely the historical development of organic chemical theory and gain thereby an appreciation of the work of the old masters.

In presenting the work to an American public it has seemed desirable to stress wherever possible the contributions of American investigators. With this end in view the chapter on "Molecular Rearrangements" has been completely rewritten and a large amount of additional material has been introduced (covering the work of Stieglitz and co-workers at Chicago University and of Wheeler and Johnson at Yale).

Several entirely new chapters have been added to those already included in the German text. The chapter on "The Theoretical Speculations of John Ulric Nef" represents Nef's own summary of his particular theoretical speculations as published in the Journal of the American Chemical Society, and has been inserted without change or abbreviation through the courtesy of that journal. The chapter on "The Electron Conception of Valency" has been written entirely by my colleague, Professor Arthur J. Hill, for whose assistance in the correction of the final text I wish to express my sincere thanks. This particular chapter is also, for the most part, new material and embodies the work of Lewis, Fry, Falk, Nelson and others of the American school of investigators. This chapter is necessarily incomplete since limitation of time and space have prevented the inclusion of the work of Langmuir and other prominent American and English workers in the newer fields of atomic chemistry.

With a subject like organic chemistry, the literature of which is so broad and comprehensive, it is not possible to give an exhaustive review or summary of all important chemical literature. The aim has been, therefore, to incorporate into the text a record of the major lines of development with explanations, and to refer the reader to the original literature for the special details and data that may be required. It is hoped that the book will prove a valuable adjunct of every library of chemistry. Criticism of the text and any additional information pertaining to the subject matter treated will be welcomed.

In conclusion I wish to thank all my colleagues of the Department of Chemistry for suggestions and criticisms which have been offered, and also to express my appreciation of the assistance of Mr. Lawrence W. Bass of the Yale Graduate School, who has been of great help to me in checking up and confirming literature references.

TREAT B. JOHNSON.

YALE UNIVERSITY,
New Haven, Conn.
May 1, 1922.

TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES

Abbreviated Title	Journal
Abh. d. Naturf. Ges. zu Halle	Abhandlungen der Naturforschenden Gesellschaft zu Halle
Am. Chem. Jour.	American Chemical Journal
Annalen der Chemie	Justus Liebig's Annalen der Chemie
Annales Chimie et Phys.	Annales de Chimie et de Physique
Annales Chim.	Annales de Chimie
Annalen Physik	Annalen der Physik
Ber.	Berichte der Deutschen Chemischen Gesellschaft
Berzelius Jahresb.	Berzelius Jahresberichte
Bioch. Zeitschr.	Biochemische Zeitschrift
Bull. soc. chim.	Bulletin de la Société chimique de France
Chem. Centralbl.	Chemisches Centralblatt
Chem. Zeitschr.	Chemische Zeitschrift
Chem. Zeitung	Chemische Zeitung
Chemie der Jetztzeit	
Chem. Abstr.	Chemical Abstracts
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences
Drude's Annalen	
Gazz. chim. ital.	Gazzetta chimica Italiana
Helv. chim. Acta	Helvetica chimica acta
Jahrb.	Jahresberichte über die Fortschritte der Chemie
Jahrb. der Radioaktivität	Jahresberichte der Radioaktivität
Jour. Am. Chem. Soc.	Journal of the American Chemical Society
Jour. Chem. Soc.	Journal of the Chemical Society (London)
Jour. de chemie phys.	Journal de chimie, physique, électrochimie, thermochimie, radiochimie, mécanique chimique, stoechiometrie
Jour. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry
Jour. prakt. Chemie	Journal für praktische Chemie
Jour. physikal. Chemie	Journal physikalische Chemie
Jour. Russ. Physikal. Chem. Ges.	Journal of the Physical and Chemical Society of Russia

Abbreviated Title	Journal
Monatsh. Chemie	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften
Ostwald's Klassiker	
Philos. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin)
Philos. Trans.	Philosophical Transactions of the Royal Society of London
Philippine Jour. Sci.	Philippine Journal of Science
Physikal. Zeitschr.	Physikalische Zeitschrift
Poggendorf's Annalen	Poggendorf's Annalen der Physik und Chemie
Proc. Chem. Soc.	Proceedings of the Chemical Society (London)
Rec. trav. chim. des Pays-Bas	Recueil des travaux chimiques des Pays-Bas et de la Belgique
Rev. gener. chim.	Revue générale de chimie pure et appliquée
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science
Schweigger's Jour.	Schweigger's Journal für Chemie und Physik
Sitzungsber. d. Berl. Akad. d. Wiss.	Sitzungsberichte der kaiserlichen Akadamie der Wissenschaften (Berlin)
Trans. Faraday Soc	Transactions of the Faraday Society
Wiener Monatsh.	Wiener (Monatshefte für Chemie und verwandte Theile anderer Wissenschaften)
Wiedem. Annalen	Wiedemann Annalen der Physik und Chemie
Zeitschr. angew. Chemie	Zeitschrift für angewandte Chemie
Zeitschr. anorg. Chemie	Zeitschrift für anorganische und allgemeine Chemie
Zeitschr. Elektrochemie	Zeitschrift für Elektrochemie
Zeitschr. physikal. Chemie	Zeitschrift für physikalische Chemie, Stochiometrie und Verwandtschaftslehre
Zeitschr. f. Chemie	Zeitschrift für Chemie
Zeitschr. f. Farben u. Textilchemie	Zeitschrift für Farben und Textilchemie
Zeitschr. f. Physik	Zeitschrift für Physik
Zeitschr. f. Physiol. Chemie	Hoppe-Seyler's Zeitschrift für physiologische Chemie
Zeitschr. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zeitschr. f. Chemie u. Ind. d. Kolloide	Zeitschrift für Chemie und Industrie der Kolloide (Kolloid-Zeitschrift)

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[1] Reprinted from the Jour. Am. Chem. Soc., **26**, 1549 (1904) through the courtesy of the editor.

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THEORIES OF ORGANIC CHEMISTRY

CHAPTER I

THE HISTORICAL DEVELOPMENT OF THE THEORY OF ORGANIC CHEMISTRY UP TO THE PERIOD OF THE THEORY OF TYPES [1]

The fundamental conceptions out of which the present theories of organic chemistry have developed originated in the discoveries of the French chemist, Lavoisier, in the latter part of the eighteenth century. As soon as this ingenious investigator recognized the importance of oxygen in nature he undertook, in co-operation with his students, a far-reaching investigation of all substances which were known to contain this element, and, as a result, oxygen became the point about which the chemistry of the age centered. What was combined with oxygen aroused little interest and was referred to in general as the base or radical. Thus even at that early period compounds were believed to consist of two parts, oxygen and the residue or radical, so that the very beginnings of chemical theory may be said to have been dualistic. The simplest compounds of oxygen were divided into two groups possessing opposite properties,—viz., acids and bases. Since salts are formed as a result of mixing acids and bases, this third group of compounds was believed to represent a chemical combination of the first two. According to Lavoisier, the real difference between inorganic and organic compounds was to be found in the fact that the former contained a simple, while the latter contained a complex radical. The immediate development of this theory was linked with a study of the simpler types of compounds.

The Atomic Theory was advanced to explain the laws of Simple and Multiple Proportion, and interpreted chemical action as resulting

[1] Compare Edv. Hjelt, "Geschichte der organischen Chemie von ältester Zeit bis zur Gegenwart." Braunschweig, Friedr. Vieweg & Sohn, 1916.

from the union of a number of atoms. Chemical compounds were supposed to consist of aggregates of atoms which were represented in terms of a system of concrete symbols. In harmony with Lavoisier's conceptions the Atomic Theory started as pre-eminently dualistic in character. Of the many hypotheses advanced to explain the cause of chemical combination, the one which received the most immediate as well as general acceptance was the Electrochemical Theory of Johann Jakob Berzelius. Its vogue at that time was due to the fact that it permitted the full development of the prevailing conceptions as to the cause and effect of chemical action, in such a way as to allow a convenient and comprehensive classification of both elements and compounds.

The close relation which exists between electrical and chemical phenomena was observed early in the history of chemistry, and attention had been drawn in particular to the fact that chemical decomposition and combination often accompany electric and galvanic processes. Volta's discovery that the mere contact of unlike substances was sufficient to generate electricity had aroused especial interest and this was increased by Sir Humphrey Davy's further discovery that many elements and compounds (among others, acids and alkalies) were also oppositely electrified by contact, and that the electrical tension thus generated was stronger in those cases where the chemical difference between the two substances was most marked. It was observed, further, that in cases where contact resulted in chemical combination all signs of the presence of electricity disappeared. Because the energy which is set free by the neutralization of elective charges may be sufficiently intense to give rise to the phenomena of heat and light, the question naturally arose in these early days as to whether the forces at work in electrical neutralization might not be analogous to those associated with chemical neutralization, since the latter phenomenon is also frequently productive of the same results. In both cases it was assumed that opposing forces counteract each other, and it therefore seemed reasonable to interpret chemical combination,—as for example, the neutralization of acids and bases,—as dualistic in the same sense as electrical processes were regarded as undoubtedly dualistic. Furthermore, since it was the custom at that time to assume that similar phenomena were due to similar causes, the question was also raised as to whether the phenomenon of flame (light) was not directly due to electrical discharge in the case of chemical combination just as in the case of the union of positive and negative electricity. Berzelius weighed all these questions very shrewdly and cleverly, and came to the conclusion that in every chemical combination a neutralization of positive

and negative electricity takes place, and that during this process the phenomena of flame (light) may be produced in exactly the same way as in the discharge of Leyden jars, galvanic piles, etc., the only difference being that in the latter case the phenomenon is not accompanied by chemical union.[1]

Davy had already transferred the seat of both positive and negative electricity (i.e., chemical affinity) to the atoms of the elements, but he assumed that the atoms became oppositely electrified only upon their approach to each other. Berzelius, on the other hand, supposed that the electric charge was inherent in the individual atom, and to a certain extent concentrated at definite points or poles. He also supposed that, just as, in general, bodies which are oppositely charged with electricity, neutralize their charges on contact with each other, so also oppositely charged atoms can discharge their electricity and in so doing unite to form chemical compounds. Thus, for example, oxygen combines with sodium because the atoms of the former element possess free negative electricity which attracts the free positive electricity of the sodium atoms. Sodium oxide, which is formed in this way, may still possess free positive electricity, and the reason for this is to be found in the fact that the quantity of free negative electricity present on the oxygen atom is not sufficient to completely neutralize all of the free positive electricity present on the sodium atom. Thus the assumption was made that the atoms of the different elements possess different amounts of free electricity and, in conformity with this idea, Berzelius arranged a series of elements in which oxygen stood first as the most electro-negative element, followed by sulphur, nitrogen, and other transitional elements over to the most electro-positive elements sodium and potassium.

In this series of Berzelius', sulphur came immediately after oxygen, and yet it was observed that these two strongly negative elements showed a pronounced chemical attraction for each other. In order to explain this apparent anomaly, Berzelius assumed that each atom of an element possesses two opposite electrical poles, provided with different quantities of positive and negative electricity, so that in any given atom there is always present a surplus of one or the other kind of electricity, and the atom appears either positive or negative according to its predominating polarity, or, in other words, it is specifically unipolar. It was by virtue of their opposite polarities that the atoms of elements combined. The simple combinations of positive and

[1] J. J. Berzelius "Versuch über die Theorie der chemischen Proportionen und über die chemischen Wirkungen der Electrizität," etc. Translated by K. A. Blöde, pp. 75 and 79, Dresden, 1820.

negative elements furnished compounds of the first order. Since the electrical charges in these compounds were not necessarily neutralized, there might remain a surplus of positive or negative charges which would enable them to enter into further combination, forming compounds of the second order. Thus, for example, sodium oxide, formed by the union of sodium and oxygen, is a compound of the first order possessing free positive electricity, while SO_3, formed from sulphur and oxygen, is a compound belonging to the same order but possessing free negative electricity. It is obvious that these two compounds may in turn combine, by virtue of their opposite polarities, to form sodium sulphate (SO_3NaO).[1] It follows according to Berzelius[2] that sodium sulphate is not formed from sodium and sulphuric acid but from sodium oxide and sulphur trioxide, which in turn may be decomposed into electro-positive and electro-negative components. The positive and negative electricity in sodium sulphate might still remain unneutralized, and it could thus combine with other similar substances of opposite polarity to form compounds of the third order (double salts).

As soon as Berzelius discovered that the fundamental laws which govern the combination of elements to form inorganic compounds apply also to the formation of organic compounds, he gave his attention to the task of interpreting the chemistry of animal and plant products in terms of the dualistic electrochemical theory. He reasoned that the only difference between inorganic and organic substances was to be found in the fact that the former consist of simple radicals while the latter consist of complex radicals in union with oxygen.[3] The same laws of cause and effect governing chemical combination hold for both classes of bodies. This conception was called upon to give the first successful impulse to the interpretation of the structure of organic compounds and has led without interruption to the enormously complex theoretical development with which organic chemistry confronts us at the present time.

The first convincing evidence of the existence of a compound radical was brought forward by Liebig and Wöhler[4] in their classical memoir entitled " Experiments on the Radical of Benzoic Acid." This recounts the investigation of a large number of substances in which the residue $C_{14}H_{10}O_2$ remains unchanged, as for example benzoic acid, $C_{14}H_{10}O_2 \cdot O \cdot H_2O$, benzoyl chloride, $C_{14}H_{10}O_2Cl_2$, benzoyl cyanide, sulphide,

[1] Old atomic weights.

[2] Versuch über die Theorie, etc., pp. 103 (1820).

[3] Kekulé, " Lehrbuch der organ. Chemie," Vol. I, 62.

[4] Annalen der Chemie, **3**, 249 (1832).

amide, etc. This was followed by the discovery of other radicals, and just as benzoyl came to be recognized as the radical of benzoic acid and its derivatives, so ethyl became identified with alcohol and its derivatives while cyanogen was seen to be the common constituent in the various cyanogen compounds. In short it became possible in the light of these new conceptions to consider a whole series of separate phenomena from the vantage ground of a common point of view.

Soon after this, Dumas made a remarkable discovery. He found that when chlorine acted upon certain organic compounds such as wax, turpentine, etc., hydrogen was removed from the substance and an equivalent amount of chlorine was substituted. In 1835 Laurent asserted that the chlorine atom assumed the same position in the molecule as had been occupied by the hydrogen, playing to a certain extent the same rôle, and that, therefore, a chlorinated compound should be similar in its properties to the body from which it was derived.[1] This idea was distinctly incompatible with the dualistic electrochemical theory and in open contradiction to its fundamental hypothesis How could the strongly electro-negative chlorine take the place of the electro-positive hydrogen or play the same rôle? The violent protestations of Berzelius induced Dumas to refute the assertion of Laurent that chlorine took the place of the hydrogen in the molecule, but he was unable to maintain his contention. The phenomenon of substitution was soon discovered to be a very general and widely disseminated law of nature and further investigation by Dumas, Laurent and others showed that hydrogen was replaceable not only by chlorine but also by bromine, iodine, oxygen and even by carbon. Indeed the marked similarity between trichloracetic acid and acetic acid led Dumas himself to assert that in this case chlorine occupied the place of hydrogen in the molecule and played the same rôle. Furthermore, he now made the absolutely general assumption that compounds which are formed as the result of substitution, still possess the same fundamental or type groupings as the compounds from which they are derived. This conception represents the beginning of the so-called "Theory of Types."

Dumas suggested an analogy between the parts composing a chemical compound and the parts of a planetary system, assuming that in both cases the components are held together by the exercise of mutual attraction. In the constitution of the compound the parts may be simple atoms or composite radicals and play the same rôles respectively as Venus and Mars, or, as the Earth with its Moon and Jupiter with its satellites. If in such a system one part is replaced

[1] Annales chimie et phys. (2) **53**, 384 (1833).

by another of a different kind, equilibrium is still maintained and if the replaced and substituting elements resemble each other, the new compound has properties similar to those of the compound from which it is derived. If, on the other hand, the elements are different, the two compounds, while belonging to the same mechanical system, show little resemblance to each other in their chemical properties. Thus in 1839 Dumas fully subscribed to a doctrine which was in absolute contradiction to Berzelius' theory of a binary arrangement of parts, and which completely ignored electricity as the force uniting the atoms of a compound. This doctrine was frequently referred to as the "Unitary Theory" to distinguish it from the Binary or "Dualistic Theory" of the Swedish chemist.

It is to be noted that only two years previous to this time, in 1837, all European chemists of prominence, and among them Dumas,[1] had signified their desire to make the electrochemical radical theory the foundation for, and the guiding principle of, all future observations in organic chemistry. It is therefore pertinent to consider the attitude of the chemists of other nations after discord had been introduced into the international concert by members of the French school.

Berzelius was not at all inclined to subscribe to the views of Dumas, since they signified for him the overthrow of the entire structure of chemical knowledge, and he even went so far in his opposition as to deny vehemently the possibility of substituting chlorine, iodine, or even oxygen, for the electro-positive hydrogen. In regard to oxygen derivatives he wrote: "A radical cannot be an oxide. The very meaning of the word radical indicates that it represents a body which is in union with oxygen. To regard a radical as an oxide would be equivalent to supposing that sulphurous acid (SO_2) is the radical of sulphuric acid, and manganese dioxide (MnO_2), the radical of manganic acid."[2] To apply this conception consistently it was necessary for Berzelius to eliminate chlorine as well as oxygen and to include only carbon, hydrogen and nitrogen as the constituents of an electro-positive radical. Thus benzoyl, $C_{14}H_{10}O_2$, the radical of benzoic acid originally accepted by Berzelius, was now replaced by the expression $C_{14}H_{10}$, and the oxide and acid became respectively $C_{14}H_{10}O_3$ and $C_{14}H_{10}O_3+HO$. Analogous changes were made in the case of acetyl and other acid radicals. A difficulty was presented by bodies which contained both chlorine and oxygen, and in such cases it became necessary to double and sometimes to treble the original molecule. Thus benzoyl chloride was written as:

$$2C_{14}H_{10}O_3+C_{14}H_{10}Cl_6$$

[1] Compt. rend., 5, 567 (1837). [2] Lehrbuch, 5th Ed. Vol. I, p. 674.

According to this conception of constitution all such radicals were supposed to be capable of an independent existence, and might therefore be isolated. It is not necessary to point out further how fundamentally different were these radicals and the rôle which they played from our present conceptions in regard to them.

The followers of Berzelius and of the "Radical Theory" were by no means unanimous in subscribing to his individual interpretations. Liebig in particular gave repeated expression to his dissatisfaction as to the manner in which Berzelius forced all the phenomena of organic chemistry into his very rigid system.[1] In connection with the mutual substitution of electrically opposite atoms he pointed out most convincingly that in inorganic chemistry the manganese in permanganic acid may be replaced by chlorine to give perchloric acid, and that the new compound shows very little difference from the old in its reaction with bases. He saw no reason for refusing to assume the presence of oxygen in organic radicals and therefore held to the benzoyl radical $C_{14}H_{10}O_2$ in interpreting the transformations of benzoic acid $C_{14}H_{10}O_3+Aq.$, and its derivatives. In 1843, in his textbook,[2] Liebig defined organic chemistry as the chemistry of the compound radical. In describing the properties of acid radicals, he says, that they combine with oxygen and with sulphur to form acids and even with hydrogen in many cases to form hydrogen acids. Among acid-forming radicals he includes certain compounds of carbon with oxygen (the oxides of carbon), cyanogen, benzoyl, cinnamyl, salicyl, acetyl, formyl, etc., and among the base-forming radicals, ethyl, methyl and others.[3]

The great majority of German chemists of this period accepted Liebig's definition of organic chemistry and, further, assumed that radicals were present as separate individual components in the molecules of the various compounds containing them. Although the statement was made in regard to radicals that only a few actually existed and that they were for the most part hypothetical, it was made in the sense that only a few radicals had as yet been isolated.[4] As a result, chemists were occupied for many years in an effort to obtain free radicals.[5] These attempts, although they failed to attain their immediate objects, were, nevertheless, valuable in leading to the discovery of many interesting substances.

While Liebig and his followers had emancipated themselves from many of the speculations of Berzelius, they continued to hold definitely

[1] Annalen der Chemie, **31**, 119; **32**, 72 (1839).

[2] Handbuch der organischer Chemie, 1843, p. 1.

[3] Ibid., p. 8.

[4] H. Kopp. "Die Entwickelung der Chemie der neuen Zeit," p. 581.

[5] Kolbe, Annalen der Chemie, **69**, 257 (1849) and Frankland, ibid., **71**, 171 (1849).

to his dualistic electrochemical theories, and at the beginning of 1840 were still in arms against the theories of substitution and the "Type Theory" as represented by the French School. Not until 1845 did Liebig himself accept the unitary conception of the constitution of the molecule.[1]

So much bitterness arose as the result of the discussions which engaged the attention of chemists of the opposing schools that each of the contending parties ended by completely ignoring the views of the other. Since, however, there was something fundamentally true in the conceptions for which each was fighting, what actually resulted was that each side unconsciously assimilated the ideas of the other, and developed them to meet its own needs. Thus, as has been seen, Liebig incorporated the idea of substitution into the Radical Theory of Berzelius. The theory of the opposing school underwent a corresponding modification; the adherents of the Type Theory had ceased using the dualistic method of writing formulas (corresponding to the Electrochemical Radical Theory) and had substituted empirical formulas for them, the latter being based upon Dumas' conception of the stellar grouping of atoms in the molecule and corresponding in essentials to the formulas in use at the present time. Following this, however, Gerhardt discovered, as a result of a study of double decomposition reactions in organic chemistry, that only certain atoms and groups of atoms present in the molecule take an active part in these processes, and that the "residue" passes unchanged from one molecule into another. Thus the idea of radical was resurrected under a new name, which was free from all dualistic electrochemical taint and which eliminated the conception of the independent existence of the residual group.

As new classes of organic compounds were discovered, as for example the polybasic acids, the chlorinated and brominated anilines, and the substituted amines, and as the effort was made to interpret all new phenomena in terms of a single theoretical conception, it became evident that the Type Theory, used in conjunction with the idea of *Residues*, afforded a simpler and more natural instrument than the Dualistic Electrochemical Theory. In the course of time the older Type Theory merged with the Radical Theory stripped of its dualistic trappings, and from the elements of this combination Gerhardt developed a new Type Theory by means of which it was not only possible to systematize all known phenomena, but also to discover new compounds and even in many cases to predict properties.

Gerhardt arranged organic compounds in four groups which were

[1] Kopp, p. 626.

referred to four simple inorganic types, namely, water (H_2O), hydrogen (H_2), hydrochloric acid (HCl), and ammonia (NH_3). In the following scheme each member of a vertical series is derived from the type by replacing the hydrogen by radicals:

H·H Type	HCl Type	HOH Type	Type
Ethyl hydride, $C_2H_5 \cdot H$	Ethyl chloride, $C_2H_5 \cdot Cl$	Ethyl alcohol, $C_2H_5 \cdot OH$	Ethyl amine, $C_2H_5NH_2$
Diethyl, $C_2H_5 \cdot C_2H_5$	Acetyl chloride, C_2H_3OCl	Ethyl ether, $C_2H_5OC_2H_5$	Diethylamine. $(C_2H_5)_2NH$
Aldehyde, $C_2H_3O \cdot H$	Benzoyl chloride, C_8H_5OCl	Acetic acid, $C_2H_3O \cdot OH$	Triethylamine, $(C_2H_5)_3N$

To these four original types of Gerhardt's, Kekulé later added a fifth, methane. Thus, for quite a period of time, chemists abandoned themselves to the amusing task of assigning newly discovered compounds to their proper places as representatives of one or another of these types. It was possible to determine, by means of double decomposition reactions, the fundamental type from which a given substance might be regarded as derived and also the radical which supposedly replaced the hydrogen in the original molecule representing the type. In this way the properties of the substance could be derived genetically from the properties of the ancestral form.

Williamson's conception of "Polyatomic Radicals" played an important part in the later development of the type theory. These were residues capable of replacing two or more hydrogen atoms in a given type. When the hydrogen atoms replaced by such radicals were present in different molecules, "Multiple or Condensed Types" and "Mixed Types" were formed. According to this conception, for example, sulphuric acid, HO—SO_2—OH, may be regarded as formed by the condensation of two molecules of water and sulphur trioxide, while oxamic acid, NH_2—C_2O_2—OH, represents a mixed water and ammonia type. Many other cases might be mentioned to illustrate Williamson's conception of organic combinations.

CHAPTER II

THE EARLY HISTORY OF STRUCTURAL CHEMISTRY

In the course of the development of the Type Theory, attention was completely diverted from the atoms and the forces acting between atoms, and became absorbed in the construction of images representing the various forms of combinations of the elements in the different compounds. Formulas were used to express not the relative position of the atoms in the molecule, but merely the reactions of the molecules and their relations as developed in the processes of double decomposition.[1] It was thought that the nature of a substance was to be inferred from a study of classes and kinds of substances, and the conception of atoms received very little support from chemists in general. In other words, the original idea—developed by Berzelius and founded upon Dalton's hypothesis—that compounds were built up primarily from oppositely electrified atoms, was either neglected or rejected by chemists. There were, of course, strenuous protestations from some quarters, to the effect that the highest aim of science could never be to derive the properties of chemical compounds from their positions in a mechanical system, and that true insight into these properties was to be gained only from a study of the atoms themselves. Frankland, and later Blomstrand, were both instrumental in redirecting attention to the electrochemical character of the atoms, but it was not until 1858 that any substantial progress was made.

It has been noted that with the passage of time the conception of the radical changed, that it ceased to represent a group capable of an independent existence and came to signify merely a residue which usually passed unaltered from one substance to another, but which in certain reactions might even suffer slight modifications in its composition. When it was finally discovered that individual radicals could be completely broken down as a result of more drastic reactions, interest was aroused once more in the elements out of which the radicals were built up. " In the present state of chemical knowledge I regard it as both necessary and possible to explain the properties of compounds from the nature of the elements composing them. I do not consider

[1] Kekulé, Textbook, Vol. I, p. 92.

that the most important task of the age is to demonstrate the presence of certain groups of atoms, or radicals, in new compounds and in this way to relate all compounds to a few types which have little significance beyond that of serving as models. Investigations should be extended to a study of the constitution of the radicals themselves. The relation of one radical to another should be carefully determined and the nature both of radicals and of the compounds which they constitute should then be referred back to the character of the elementary atoms." With these words Kekulé[1] redirected the attention of chemists to the fundamental conception of the atom. He was able to hold their attention by further developing the conception of " Basicity " or " Atomicity."

Even in the time of Berzelius it was customary to speak of the " saturation capacity " of acids and bases, understanding by this the ability of these substances, under quite definite conditions, to combine with each other. Frankland[2] extended this idea to the atoms of the elements, and, in co-operation with H. Kolbe and others,[3] amplified it somewhat. The elements N, P, As, and Sb, for example, form chemical compounds in which either three or else five equivalents of other elements are always found. The affinity of a single atom of the elements in question is thus always satisfied by a specific number of other atoms. The ability of an atom to combine with a definite number of other atoms or groups of atoms was referred to as the " Atomicity " or " Basicity " of the element, and is fundamentally the same as the term " Quantivalence " recently suggested by A. W. von Hofmann.

Kekulé adopted this conception and amplified it. In 1857 he pointed out that H, Cl, Br, K and others belong to the monatomic elements; S and O to the diatomic; N, P, As, etc., to the triatomic elements. A year later he extended his speculations to carbon. In working out the application of the conception of atomicity to this element he laid the foundations for future important developments in the theory of Organic Chemistry.[4] He wrote as follows: " If the simpler compounds of carbon are examined as, for example, CH_4, $CHCl_3$, CH_3Cl, CCl_4, CO_2, $COCl_2$, CS_2, HCN, etc., it is obvious that one atom of carbon always combines with four monatomic or with two diatomic atoms. In other words, the sum of the units of

[1] Annalen der Chemie, **106**, 136–137 (1858).

[2] Ibid., **85**, 368 (1858).

[3] See E. von Meyer, " Geschichte der Chemie," 3d Edition 1905, p. 286, and Hjelt l. c., p. 287.

[4] Annalen der Chemie, **106**, 153–154 (1858).

affinity by means of which carbon combines with other elements is always four, and this leads to the belief that carbon itself is tetra-atomic (tetrabasic)." In relation to the three groups of other elements which have been mentioned, carbon takes its place as the representative of a fourth group.

It should be noted that in accepting the idea of atomicity and applying it to carbon, Kekulé used the term in a sense essentially different from his predecessors—that is to say, he assumed that atomicity was an absolute constant. At that time he had good reasons for making this assumption. Dalton's Atomic Theory, taken by itself, was able to explain only the Law of Definite Proportions, and afforded no adequate interpretation as to why the different elements always combined in definite multiple numbers and not irregularly. In order to explain logically the Law of Multiple Proportion, it was necessary to add to Dalton's original theory the further assumption of Atomicity. This fact led Kekulé to conceive that the property of *constant* atomicity was a fundamental property of the atoms, and as unchangeable as the atomic weights themselves.

Thus in 1858 a new theory in regard to the nature of chemical combinations had its rise, and by 1864, Kekulé[1] had formulated this theory in a way which allowed of its very general application. In the course of time a great number of theoretical speculations which had been advanced by other chemists—as, for example, Frankland, Kolbe and Erlenmeyer, Sr.—were first modified and then merged into Kekulé's theory, so that it became, as it were, the cradle of structural chemistry. It may be briefly summarized as follows:

The molecules of chemical compounds consist of atoms which are held together by a special kind of attraction. Many atoms have only one center of attraction while others have several such centers, and they may, therefore, be classified as mono- or multi-atomic. In all combinations of atoms the units of affinity of a given atom are saturated wholly or in part by an equal number of units belonging either to one or to several other atoms. Atoms may combine with other atoms of the same kind or of different kinds. By means of these assumptions it is possible to explain why many elements seem to show a variation in valency toward others. In the case of substances which contain several atoms of carbon, for example, it is necessary to assume that the carbon atoms are mutually bound to each other and that, therefore, only a part of the affinity of each is available for holding other kinds of atoms within the molecule.[2]

[1] Compt. rend., 58, 510 (1864).

[2] Annalen der Chemie, **106**, 154 (1858).

The compounds in which the atoms are mutually held together by means of their affinities are called " atomic " or true chemical compounds, and their molecules are stable in the gaseous state. Kekulé distinguished between atomic and molecular compounds. The latter may be obtained from the former in the following manner: When the molecules of different atomic compounds react, the atoms constituting one molecule may exercise an attraction for the atoms constituting the other. This mutual affinity causes the two molecules to draw together and to unite. The process is often preliminary to chemical decomposition, in which case the addition of the two molecules is only temporary and is accompanied by a rearrangement of the atoms. Where rearrangements of the atoms are impossible because of the nature of the two molecules, the union may be permanent and the two molecules may cling together forming a more or less stable group. The relative stability of such unions must necessarily be less than in the case of atomic compounds, and this explains why " molecular " compounds do not vaporize as such, but on heating decompose into the simpler compounds from which they were formed. Ammonia and phosphorus trichloride were regarded by Kekulé as examples of atomic compounds, while $NH_3 \cdot HCl$ and $PCl_3 \cdot Cl_2$ were classed as molecular compounds.

The theory of Kekulé was subject to vehement attack even in the very beginning of its development. The students and followers of Berzelius held firmly to the view that chemical combinations were due to the action of positive and negative electrochemical forces. and that, therefore, the valency of the elements was not a constant but a variable quantity. Hermann Kolbe stood foremost among the opponents of Kekulé's views. He assailed them to the very end of his life with the full force of his impressive personality and with powers of discernment which were far greater than those usually exercised in scientific controversy. But in seeking to establish the law of electrochemistry as the causal factor in promoting chemical change, he actually defeated his own ends by his very vehemence; for Kekulé and his followers ceased, as it were by common agreement, to reply to his charges, and the law of electrochemistry was almost completely ignored. Kekulé's theory of the constancy of valency was not accepted, however, without other challenge.

In 1856 Gerhardt concluded from a study of the compounds of nitrogen that this element exercises sometimes three and sometimes five valencies. Variation in the valencies of other elements had been discovered by Frankland, Williamson, Couper, Kolbe and others, and the opinion had even been expressed that carbon functions as a

bivalent element in ethylene, acrylic acid and other compounds. As a result of these investigations the Theory of Maximum Saturation Capacity had its rise, and it was in part at least in opposition to Kekulé's hypothesis. In terms of this new conception, the atoms of all the elements possess a definite limiting number of affinities by means of which they may attract the atoms of other elements. The greatest number of valencies which one atom of an element may bring into play is called the " Maximum Saturation Capacity " of that element. In the case of nitrogen and of carbon, this number is represented by five and four respectively. Compounds in which two elements function to the limit of their powers (NH_4Cl, $CHCl_3$, etc.), were regarded by Erlenmeyer, Sr., as saturated compounds. In many compounds, however, the elements do not exercise their maximal powers of affinity (NH_3, C_2H_4, C_2H_2, etc.) and such compounds were regarded by Erlenmeyer, Sr., as " unsaturated." Kekulé opposed the Theory of Maximum Saturation Capacity [1] and held firmly to his assumption in regard to the absolute constancy of valency, attaching to it the importance of a fundamental law of nature.

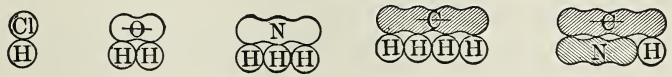
In the subsequent historical developments neither conception gained complete acceptance. The idea of maximum saturation capacity was more or less neglected until quite recently, when it was resurrected again; but, on the other hand, variation in the basicity of at least some elements (as, for example, nitrogen) came to be more and more generally accepted. Kekulé did succeed in impressing the great majority of his fellow chemists with the belief in the constant valency of carbon. He accomplished this by reason of his influence on the development of structural chemistry.

After the distinction between atom and equivalent had been clearly demonstrated by Cannizarro, an attempt was made by Butlerow, Erlenmeyer, Kekulé and others to gain deeper insight into the structure of chemical compounds. Butlerow was the first investigator to use the expression " the structure of a chemical compound " although Erlenmeyer, writing at about the same time, used the term " constitution " to express the idea of the mutual relation existing between the atoms in a molecule. Butlerow may indeed be said to have outstripped Kekulé, in so far as he discerned in 1860, that the future task of chemists was to be that of determining " the nature and the manner of the mutual union of the atoms in the molecule."

In 1861 Kekulé began to use graphic formulas. He was able to attack successfully the problem of representing the relations of the atoms in the molecule by assuming, first, the tetravalency of carbon

[1] Kekulé's " Lehrbuch," I, pp. 160 and 162; Compt. rend., **58**, 512 (1864).

in all of its compounds, and second, the ability of carbon atoms to combine with each other by means of one or more units of affinity. In amplifying the atomic pictures used by Berzelius, atoms of different basicity (atomicity, valency) were represented as of different size. Thus hydrogen chloride, water, ammonia, methane and hydrogen cyanide were represented by the following graphic formulas:[1]



These symbols, although long since abandoned, signified a very important step forward at that time, since they made it possible to picture the exact relation of the atoms in the molecule, and they represent the direct transition from the theory of types to the theory of structural chemistry. Soon after this the letters B, C, N, O, H, etc., were used by Erlenmeyer, Sr., to denominate the different elements, while dashes were added to signify the number of units of affinity (valency) in any given case. This method of representation gradually took the place of the graphic formulas. Thus, by about 1870, structural or constitutional formulas began to be used in much the same form as at the present time.[2]

Kekulé was able to demonstrate the constant valency of carbon in saturated compounds without much difficulty, but the matter was not quite so simple in the case of the unsaturated compounds. At first he merely assumed that the carbon atoms present in compounds of the latter type were in much closer union than was the case in saturated compounds, and made no attempt to explain the nature of this union. But later, when he had become convinced, as a result of experimental investigations in the field of unsaturated acids, that ethylene and its derivatives really show the properties of unsaturation and are able to add H_2, Br_2, etc., with great ease, he evolved the hypothesis "that two units of affinity of the carbon are not saturated, and are therefore, in a sense, present in the molecule in a free state."[3] Or again: "At those positions in the molecule where hydrogen atoms are lacking, the two units of affinity of the carbon atoms remain unsaturated and in a sense there is a void. It is not difficult, therefore, to understand why substances of this type add hydrogen and

[1] Lehrbuch, I, pp. 160–162.

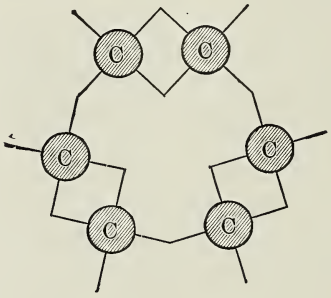
[2] For a history of the development of graphic formulas see Anschutz, Zeitschr. angew. Chemie, **27**, 323 (1914).

[3] Lehrbuch, II, p. 251.

bromine with such ease. The free units of affinity have a tendency to become saturated and so to fill this void."[1]

Kekulé soon abandoned these assumptions, and the very volume of his textbook from which these quotations have been taken, contains suggestions which form the nucleus for theories which are held at the present time. Since these theories are intimately connected with Kekulé's conception in regard to the constitution of benzene, a consideration of this subject is now in order.

Kekulé started with the assumption that aromatic compounds in general are to be regarded as derivatives of benzene, since in even the most drastic reactions one product is always aromatic and contains at least six carbon atoms. To explain the aromatic structure of these substances on the basis of the tetravalence of carbon, it was necessary to evolve an essentially new hypothesis, and he conceived that the six carbon atoms, common to all such compounds, were bound together not in an open chain but in the form of a closed ring. He conceived, further, that they were held together in this way by the mutual exercise not of two, but of three affinity units (valencies) each. The following graphic formula, published in 1865, pictures for the first time double bonds and a ring of six carbon atoms:



By means of this hypothesis it was obviously possible to express the mutual relations of the atoms in the molecule without abandoning the idea of the tetravalence of carbon.

From this time " structural " or " constitutional " formulas came into more and more general use, and they were found to be quite as serviceable as the formulas of the " type theory " in correlating and systematizing the innumerable organic compounds which were being discovered. Indeed, the new formulas did more, in that they afforded an insight into the mutual relationships of the atoms within the molecule, or, in other words, into its internal structure.

[1] Lehrbuch II, p. 259.

Structural formulas were especially helpful in interpreting numerous instances of isomerism, since almost all were explicable on the assumption of differences in the arrangement of the atoms in the molecule. In the case of one relatively small group of isomeric substances, however, structural formulas proved to be inadequate to explain the observed differences in properties. This was the group of "physical isomers," so named by Kekulé because, while corresponding very closely as to chemical properties, these substances were often almost exactly opposite in physical properties. Thus, while one isomer turned the plane of polarized light a definite amount to the right, the other either turned the plane of polarized light exactly the same amount to the left or else had no effect whatever upon it. To this group of substances belonged tartaric acid, aspartic acid, malic acid and others. Toward the solution of the problem offered by these substances, the classical researches of Pasteur had already yielded results of fundamental importance. In 1869 Johannes Wislicenus added lactic acid to this series of "physical isomers," demonstrating beyond the shadow of a doubt that the lactic acid obtained from sour milk and the so-called "sarco-lactic acid" were both α-hydroxypropionic acid, and therefore corresponded to the structural formula

$$CH_3CHOHCOOH.$$

"The isomeric lactic acids offer the first authentic case where the observed number of isomeric substances exceeds the structural possibilities," and Wislicenus goes on to observe that "Facts of this sort can be explained only by supposing that the difference in the isomeric molecules is to be accounted for by a difference in the spacial arrangement of their atoms."[1] Thus, eight years after Butlerow (1861) had emphatically denied that his conception of the term "structure" included the idea of space relationships, J. Wislicenus and Blomstrand were able to show the necessity for this further extension of the theory of atomic relationships. The problems of physical isomerism were not, however, solved at this time but were temporarily neglected, because for the moment the concentrated effort of the majority of chemists was bent upon the solution of the more immediate problems of structural chemistry, as, for example, those involved in the chemistry of benzene. Nevertheless, by 1874, the phenomena of physical isomerism had found a master interpreter in the person of Jacobus Henricus van't Hoff.

[1] Annalen der Chemie, **167**, 343 (1873).

CHAPTER III

LATER DEVELOPMENTS IN STRUCTURAL CHEMISTRY

It was Jacobus Henricus van't Hoff who finally solved the problems presented by the phenomena of physical isomerism. He was able to do much more than meet the immediate difficulties of the times in which he lived, for his researches in the field of Thermodynamics led him to conceive the matter in terms so fundamental and far-reaching that their full significance has only recently been recognized. Van't Hoff gained his first knowledge of the theory of structural chemistry at Bonn under the leadership of Kekulé himself, while later in Paris he became conversant with the classical researches of Pasteur on the isomerism of the tartaric acids.[1] Thus his theoretical conceptions were from the beginning subject to these two particular influences.

"Modern chemical theory has two weak points; it fails to consider the relative position which the atoms occupy in the molecule and also the nature of their motion." This is the opening sentence of the German translation of van't Hoff's classical treatise entitled "Die Lagerung der Atome in Raume." The conceptions set forth in this text are in a certain sense more fully and exhaustively treated in the book entitled "Ansichten über Organische Chemie,"[2] by the same author. In both books van't Hoff emphasized the two fundamental weaknesses in chemical theory which have just been mentioned. He was the first to feel the necessity of representing the four valencies of carbon as directed toward the four corners of a tetrahedron at the center of which the carbon atom was assumed to be located. It must be noted that this conception of the distribution of the valencies of carbon is quite different from the original conception, which supposes that all four valencies of carbon lie in the same plane.[3] On the assumption of van't Hoff it is possible to explain the phenomena of physical isomerism observed in the cases of lactic, malic, tartaric acids, etc., by supposing that the difference in the properties of the isomeric

[1] E. Cohen, "Jac. Henr. van't Hoff," p. 12, Leipzig, Engelmann, 1899.

[2] Braunschweig, Friedr. Vieweg und Sohn, 1878.

[3] Kekulé also made use of atomic models to illustrate atomic constitution as early as 1867. See Zeitschr. f. Chemie, N. F. 3, 218.

substances is due to a difference in the arrangement of the atoms in space. The science of stereochemistry [1] was thus founded upon van't Hoff's conceptions in regard to the asymmetry of carbon, and following this time it developed steadily although not rapidly. It can be referred to here only in so far as it is related to the evolution of structural theory in general.

In the year 1885 A. von Baeyer succeeded in establishing a logical basis for many previously unfounded assumptions in regard to the constitution of organic compounds by interpreting them in terms of the new conception of the carbon atom. His work had a directing and most fruitful influence upon research, and demonstrated what real progress might be made on the basis of van't Hoff's assumption.

Kekulé explained the constitution of benzene by assuming that the six carbon atoms were joined together in the form of a ring, and this idea was later extended to explain the constitutions of pyridine, quinoline, naphthalene, thiophene, pyrrol, tri-, tetra-, penta-, and hexamethylene, and other cyclic combinations. The assumption of ring structure in these cases, while offering an illuminating interpretation of the relative stability of the substances, was nevertheless arbitrary. There was no really logical ground for supposing ring formation, and because of this fact numerous objections were raised against Kekulé's formula for benzene.

A. von Baeyer,[2] in logically developing his "Theory of Tension" for ring compounds on the basis of the new space model for the carbon atom, succeeded in meeting some of these objections. He reasoned that, on the basis of van't Hoff's assumption, the angle formed by the mutual union of the valencies of any two carbon atoms must be 109° 28′. If other carbon atoms are now imagined as joined successively to the first pair, in such a way that their centers of gravity all fall within the same plane, it will be found that these atoms must arrange themselves either in a zig-zag line or a ring form, supposing only that the fixed angle be maintained. By referring to a model constructed by joining five carbon atoms in a chain of this sort, it becomes apparent that a valence of the first atom in the series may be readily united to a valence of the fifth to form a closed ring. It is also obvious that rings of three and four carbon atoms can be formed only as the result of deflecting the direction of the combining valencies away from their normal angles of 109° 28′. The resistance offered by the valencies of carbon atoms to deflection from their fixed positions around the atom shows

[1] Compare Textbooks of Stereochemistry by van't Hoff, Hantzsch, Bischoff-Walden, A. Werner, E. Wedekind and others.

[2] Ber., **18**, 2278 (1885).

itself in the form of a strain, and is comparable to the tension observed in the case of a bent metal spring. On the basis of such a conception it is easy to understand why rings of five carbon atoms are stable, while, on the other hand, rings of three or four are unstable.

Baeyer calculated the degree of the deflection of carbon valencies in the case of various ring structures, when the following results were obtained. The degree to which each valence is bent toward the center of the ring is

24° 44′ for the trimethylene ring;
9° 44′ for the tetramethylene ring;
0° 44′ for the pentamethylene ring;

while the degree of angular distortion away from the center in the case of the higher cycles is

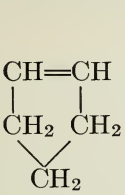
5° 16′ for the hexamethylene ring;
9° 33′ for the heptamethylene ring.

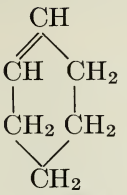
According to this conception the pentamethylene ring should be the most stable of all, and this conclusion is supported by the observation that it is, in fact, the most easily formed of all rings. It must be noted, however, that while hexamethylene rings are formed less readily than pentamethylene rings, they show a greater stability than might be expected on the basis of the theoretical considerations represented in the above table. This stability may be explained, on the other hand, by supposing that the centers of gravity of the six carbon atoms lie in different planes, in which case a model may be constructed without necessitating the deflection of any valence of carbon from the normal angle of 109° 28′. It should, nevertheless, be added that the stability of carbon rings in general depends not only upon the number of atoms, but also, and to a very great extent, upon the nature of the substituents which are in union with these atoms.

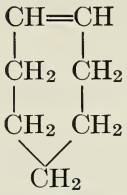
According to Baeyer's "Tension Theory," a parallel should exist between the ease with which rings are formed and the stability of the resulting compound. The number of instances where the facts are in direct contradiction to this assumption have been greatly augmented in recent years, so that the whole question as to the correctness of Baeyer's conception has been opened up anew. For example, Harries and his students [1] have succeeded in preparing a number of ozonides. These bodies represent products which are formed by the addition of

[1] Annalen der Chemie, **374**, 303 (1910); Compare also H. and C. Thieme, Ber., **39**, 2849 (1906) and H. and L. Tank, Ber., **41**, 1701 (1908); also Berger "Zur Kenntniss des l-methylcyclopentanon-3 und l-methylcyclopentene-2," Inaugural Dissertation, Kiel, 1914.

ozone to the unsaturated carbon atoms present in the following types of ring structure:

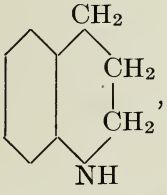

Cyclopentene

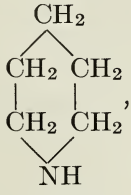

Cyclohexene

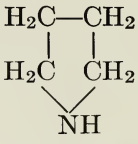

Cycloheptene

As is well known, ozonides of this class may be hydrolyzed by water when they yield oxidation products which contain open carbon chains, as for example aldehydes and acids. It would seem natural on the basis of Baeyer's conception of ring structure to suppose that the ozonide of cyclopentene would be the most stable of these derivatives and that of cycloheptene the least stable. As a matter of fact, however, this is not true, for it has been observed that the ring actually opens most readily in the case of the ozonide of cyclopentene.

Analogous phenomena have been observed by J. v. Braun [1] in connection with a study of heterocyclic compounds. A comparison of the following types shows that the pyrrolidine ring is formed most readily.


Tetra-hydroquinoline


Piperidine


Pyrrolidine

It should, therefore, in the sense of Baeyer's theory, be the most difficult to open, but such is not the case. J. v. Braun has succeeded in modifying A. W. v. Hofmann's method of exhaustive methylation in such a way as to make it of general application in opening rings of this type,[2] and a comparison of the behavior of the above and other substances has demonstrated the fact that the pyrrolidine ring opens much more readily than the piperidine ring, and that this in turn opens somewhat more readily than the tetra-hydroquinoline ring. In arranging ring-bases in the order of their relative stability both

[1] Chem. Zeitung, 1911, 374; Ber., **44**, 1253 (1911).

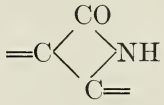
[2] Ber., **33**, **35**, **36**, **37**, **38**, **39**, **40**, **41**, **42**, See particularly **49**, 2630 (1916), and "Über die Entalkylierung und Aufspaltung organischen Basen mit Hilfe von Bromcyan und Halogenphosphor." Wallach—Festschrift, p. 313 and following.

with reference to the effects of exhaustive methylation and the action of cyanogen bromide, J. v. Braun discovered a somewhat remarkable parallelism. In both series stability increases from left to right in the following order:

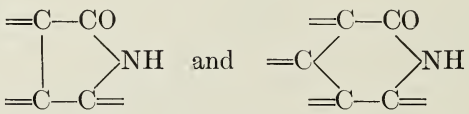
Pyrrolidine > Piperidine > Tetra-hydroquinoline

The fact that these substances behave analogously under the influence of such distinctly different types of reagents must find its explanation in something fundamental in the nature of such ring systems. While it is not yet possible to say just what this is, it must, nevertheless, be acknowledged that this action, which obviously proceeds with fairly definite regularity, cannot be explained on the basis of the theory of internal tension or strain.

In the case of heterocyclic rings which are formed by the addition of ketene, $R_2C{=}C{=}O$, to substances possessing the unsaturated group C:N, H. Staudinger [1] has observed that the stability of the ring depends not only upon the number of atoms present in the ring, but also upon the character and the interrelationships of these atoms. Thus, for example, certain β-lactams of the general formula



are practically as stable as the γ- and δ-lactams of 5 and 6 members respectively, i.e.,



It should be noted, however, that the foregoing and other exceptions to the assumptions of Baeyer's "tension theory" have only very recently come to the attention of chemists. In 1885 Baeyer's conception of the mechanism of ring formation was very generally accepted. Indeed, it seemed to follow as a logical consequence of the assumptions in regard to the nature and chemical behavior of the carbon atom which were prevalent at that time. These assumptions Baeyer [2] was able to condense into the form of seven fundamental principles which may be stated as follows:

[1] H. Staudinger "Die Ketene," p. 59, Stuttgart, Enke, 1912.
[2] Ber., **18**, 2278 (1885).

1. Carbon is usually tetravalent.

2. Its four valencies are equivalent, as shown by the fact that there is no isomerism in the case of the monosubstitution products of methane.

3. These valencies may be represented as directed toward the corners of a regular tetrahedron, constructed around the carbon atom as a center, and are, therefore, equidistant from each other in space.

4. The atoms or groups, joined to carbon by the exercise of its valencies, occupy definite and permanent positions both with reference to the central carbon atom and with reference to each other. This is shown by the fact that isomerism occurs in the case of derivatives of methane where the substituting atoms or groups—*a*, *b*, *c*, and *d*—are all different. (The law of Le Bel and van't Hoff.)

5. Carbon atoms are capable of entering into combinations with other carbon atoms by means of 1, 2 or 3 valencies.

6. The resulting compounds form either open or closed carbon chains.[1]

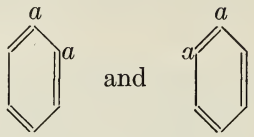
7. The four valencies of carbon, operating from the central atom in the direction of the corners of a circumscribing regular tetrahedron, diverge from each other by an angle of 109° 28′. This angle may be increased or diminished, but such a change is always accompanied by a condition of strain or tension within the molecule.

These principles follow as logical deductions from the assumptions of van't Hoff, and were accepted by the majority of chemists. With them as a basis Baeyer now proceeded to subject the much debated question of the constitution of benzene to a systematic experimental investigation. Up to this time benzene and its derivatives had been investigated and discussed principally with reference, first, to the question of the relative position of the groups substituting in the ring, and second, the question of decomposition products. These investigations had led to no definite choice between the several equally probable formulas which had been advanced to explain the various phenomena. Baeyer turned his attention to an experimental study of the gradual transformation of fatty into aromatic compounds, and of the corresponding reverse processes. The results of these researches have become classical, and form the basis for new theoretical conceptions which are among those most widely discussed at the present time.

Kekulé's formula for benzene found more general acceptance than any other proposed at that time. It is true that the assumption of alternate double and single bonds between the carbon atoms of the

[1] Compare G. Grüttner and E. Krause, Ber., **49**, 2666 (1916).

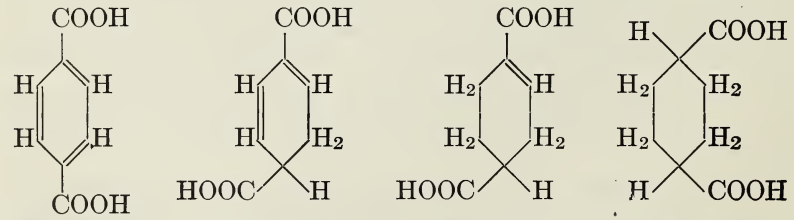
ring presupposes the existence of is omeric *ortho*-disubstitution products as for example,



and as yet no isomerism of this kind had been observed. This objection has been met in part, however, by Kekulé's "Oscillation Hypothesis."[1]

It was to be assumed from the presence of three pairs of unsaturated double bonds in the molecule that benzene would show highly unsaturated properties—i.e., that it would add hydrogen, hydrogen chloride, halogen, etc., and that it would reduce permanganate readily—and the facts of the case are in formal agreement with these assumptions. One of the first and most important tasks of Baeyer was to prove beyond the shadow of a doubt that hexahydrobenzene and hexamethylene were identical. He was careful, however, to point out a very important difference between aliphatic and aromatic compounds as shown in the ease with which they react respectively with hydrogen, halogen, etc. Thus while the great majority of unsaturated compounds of the aliphatic series form addition products readily at ordinary temperatures, aromatic compounds react slowly and require the presence of heat or sunlight. Further, benzene derivatives, having no readily oxidizable side chains show for the most part very little reactivity to permanganate and at best are only incompletely oxidized, while unsaturated aliphatic compounds are immediately attacked by this reagent even in the cold.

Differences in the behavior of benzene derivatives as compared with unsaturated aliphatic compounds were very carefully investigated by Baeyer in connection with a study of the phthalic acids. These acids, for example, react successively with two, four, and then six hydrogen atoms, giving along with others the following compounds:



Terephthalic acid | $\Delta^{1,5}$-Dihydroterephthalic acid | Δ^{1}-Tetrahydroterephthalic acid | Hexahydroterephthalic acid

[1] Annalen der Chemie, **162**, 86 (1872).

Terephthalic acid itself, in spite of its three pairs of doubly-bound carbon atoms, is very stable toward permanganate and adds halogen only with great difficulty. Upon reduction these properties abruptly change and the resulting dihydro- and tetrahydro- derivatives not only react readily with bromine, adding two and four atoms respectively, but are also so unstable in the presence of permanganate as to be mistaken for unsaturated aliphatic compounds.

These typically unsaturated properties vanish again when the process, which has just been described, is reversed and the hydro-derivatives are oxidized to phthalic acid. In this case the change from tetrahydro- to dihydrophthalic acid is accompanied by an increase in unsaturated properties such as would normally be expected in passing from a substance containing one pair of doubly-bound carbon atoms to a diethylene compound. But with the next step in the process, i.e., with the formation of a third pair of doubly-bound carbon atoms, the substance, instead of showing increased unsaturation, suddenly and abruptly loses all of the characteristics commonly associated with a condition of unsaturation in the molecule. In other words, its ability to add hydrogen, halogen, etc., has vanished, and its general stability has become comparable to that usually attributed to saturated compounds. These generalizations were arrived at by Baeyer as the result of a purely chemical investigation of the substances.

Stohmann came to the same conclusions in a different way, but in order to understand the significance of his investigations, it will be necessary to make a few preliminary remarks.[1] It is usually assumed that a certain amount of energy is stored up in every molecule that is capable of maintaining an independent existence. This is always the same in quantity for molecules of the same kind, whether of elements or of compounds. In other words, all molecules possess a definite amount of potential energy which is changed into kinetic energy (heat, electricity, etc.), when the molecules suffer decomposition into their respective atoms, as happens in the course of chemical reactions. The fact that A and B react to form C and D is expressed by the equation

$$A+B=C+D$$

but this represents the change in the energy relations very indefinitely and very incompletely. It does not show, for example, whether the energy set free by the decomposition of A and B is consumed wholly or in part by the formation of C and D. It is possible that the

[1] For recent development of this subject see Weinberg, Ber., **52**, 1501 (1919); K. Fajans, Ibid., **53**, 643 (1920); also Steiger, Ber., **53**, 666 (1920).

energy of $A+B$ may be equal to, or else greater or less than that of $C+D$. If the energy $A+B$ is greater than the energy of $C+D$, it follows that chemical action is accompanied by the evolution of heat, and that the reaction belongs to the class known as exothermal, i.e.,

$$A+B=C+D+\text{heat}$$

If, however, the energy of $A+B$ is less than that of $C+D$, energy must be added to the system in order to induce the reaction,

$$A+B+\text{heat}=C+D$$

which is now said to be endothermal in character.

In the case of unsaturated aliphatic compounds the addition of hydrogen belongs to the exothermal type of chemical reaction. Thus, for example:

$$\underset{\text{Ethylene}}{C_2H_4} + H_2 = \underset{\text{Ethane}}{C_2H_6} + 31.9 \text{ Cal.}$$

$$\underset{\text{Propylene}}{C_3H_6} + H_2 = \underset{\text{Propane}}{C_3H_8} + 32.5 \text{ Cal.}$$

$$\underset{\text{Fumaric acid}}{C_4H_4O_4} + H_2 = \underset{\text{Succinic acid}}{C_4H_6O_4} + 32.5 \text{ Cal.}$$

These reactions serve to show that approximately the same amount of heat is liberated by the reduction of a variety of unsaturated compounds.

Stohmann [1] now proceeded to determine the value for the heat liberated in the progressive reduction of terephthalic acid, and obtained the thermal values expressed below:

$$\underset{\substack{\text{Terephthalic}\\\text{acid}}}{C_8H_6O_4} + H_2 = \underset{\substack{\Delta^{1,5}\text{-Dihydrotere-}\\\text{phthalic acid}}}{C_8H_8O_4} - 2.8 \text{ Cal.}$$

$$\underset{\substack{\Delta^{1,5}\text{-Dihydrotere-}\\\text{phthalic acid}}}{C_8H_8O_4} + H_2 = \underset{\substack{\Delta^{1}\text{-Tetrahydrotere-}\\\text{phthalic acid}}}{C_8H_{10}O_4} + 28.9 \text{ Cal.}$$

$$\underset{\substack{\Delta^{1}\text{-Tetrahydrotere-}\\\text{phthalic acid}}}{C_8H_{10}O_4} + H_2 = \underset{\substack{\text{Hexahydrotere-}\\\text{phthalic acid}}}{C_8H_{12}O_4} + 23.5 \text{ Cal.}$$

These figures show that in the first stage of the process of the reduction of terephthalic acid, results are obtained which are not in harmony with the general rule which has been formulated in regard to the addition of hydrogen to doubly bound carbon atoms, since energy is absorbed and not given off in the reaction. The second and third steps in the process, on the other hand, proceed quite regularly. Further, the thermal relationships observed in the case of this particular series have been found to hold quite generally for the reduction products of

[1] Jour. prakt. Chemie, **41**, 13–14, 538 (1890); **45**, 475 (1892); **48**, 447 (1893).

benzene and its derivatives. The following values have been obtained in the reduction of benzene itself:

$$\underset{\text{Benzene}}{C_6H_6} + H_2 = \underset{\text{Dihydrobenzene}}{C_6H_8} + 0.8 \text{ Cal.}$$

$$\underset{\text{Dihydrobenzene}}{C_6H_8} + H_2 = \underset{\text{Tetrahydrobenzene}}{C_6H_{10}} + 25 \text{ Cal.}$$

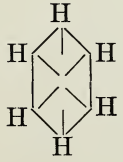
$$\underset{\text{Tetrahydrobenzene}}{C_6H_{10}} + H_2 = \underset{\text{Hexahydrobenzene}}{C_6H_{12}} + 27.8 \text{ Cal.}$$

$$\underset{\text{Hexahydrobenzene}}{C_6H_{12}} + H_2 = \underset{\text{Hexane}}{C_6H_{14}} + 11 \text{ Cal.}$$

From these results it is established that in the case of substances containing benzene nuclei the first step in the process of reduction is essentially different from the second and the third and that the latter, in their observed heats of reduction, correspond to reductions which involve the addition of hydrogen to doubly bound carbon atoms in aliphatic compounds.[1]

It thus appears that a certain amount of resistance must be overcome before the change from benzene to dihydrobenzene can take place, and that energy, which would ordinarily be set free by the addition of hydrogen, is used up in this process. After this initial reaction, further additions of hydrogen take place regularly with the usual evolution of heat. In brief, the abrupt change in properties attendant upon the formation or destruction of the benzene nucleus has been confirmed by physical as well as by purely chemical investigation.[2] Moreover, it follows that the presence of three pairs of doubly bound carbon atoms in the benzene nucleus may no longer be assumed, and that, therefore, Kekulé's formula does not correctly express the constitution of benzene and its derivatives.

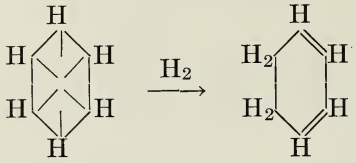
In order to account for these facts in a more satisfactory manner Baeyer discarded Kekulé's formula and substituted in its place the so-called "centric formula" which was originally suggested by H. Armstrong.[3]



According to this the fourth valency of each carbon atom is represented as merely directed toward the center of the ring (as shown by

[1] Jour. prakt. Chemie, **43**, 21 (1891).
[2] Annalen der Chemie, **407**, 145 (1915).
[3] Jour. Chem. Soc., **51**, 264 (1887).

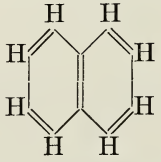
the short lines) thus indicating that by their mutual action the power of each is rendered latent, and that a condition of equilibrium is thereby established. Such a centric method of linkage is unknown in the fatty series and may be regarded as a prerogative of aromatic compounds. When benzene is reduced to dihydrobenzene this condition of equilibrium is destroyed with the saturation of two bonds, and the remaining four of the six centric bonds rearrange themselves to form two normal pairs of unsaturated double linkages:



Such a conception accounts readily for the marked difference in properties between benzene and its reduction products.

The investigations of Baeyer placed the chemistry of benzene and its derivatives in quite a new light. They led to the general conclusion that the essential characteristics of aromatic compounds depend upon the peculiar symmetrical arrangement of the fourth valency of each of the six carbon atoms present in the nucleus, and not upon ring formation nor yet upon the groupings of carbon linkages.[1] This peculiar condition was referred to later as the "latent" condition of these six valencies.

This conception of structure was soon applied to other types of cyclic compounds. In 1890 Bamberger[2] discovered that naphthalene is much more readily attacked by reducing agents than are other benzene derivatives, and that it adds first two and then four atoms of hydrogen. With the addition of four atoms a limit seems to be reached, and the further addition of six hydrogen atoms is observed to meet with a resistance similar to that observed in the initial stage of the reduction of benzene. This resistance, along with other chemical properties of tetrahydro-naphthalene, marks the first indication of a true benzene nucleus in the naphthalene molecule. Such relationships find no expression in the formula of Erlenmeyer, Sr., and Graebe,



[1] Annalen der Chemie, **257**, 47–48 (1890).
[2] Ibid., 1 and following (1890).

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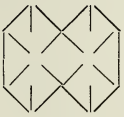
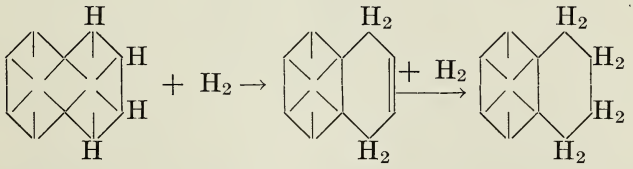
which assumes the presence of two true benzene nuclei in naphthalene. In order better to explain these facts, Bamberger applied Baeyer's idea of latent valencies centrally directed and in this way evolved the following constitutional formula for naphthalene:

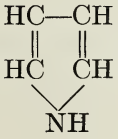


This represents two rings in each of which are present six latent valencies similar in character to those represented by the centric formula of benzene. At the same time it should be noted that neither ring represents a true benzene nucleus. The action of reducing agents may be supposed to destroy the condition of equilibrium in this system, and the saturation of four of the original ten latent valencies brings about a rearrangement which results in the formation of a true benzene nucleus:



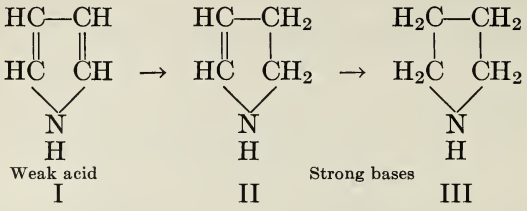
The relationships expressed by these formulas show why the benzenoid character of the substance is accentuated by reduction — tetrahydronaphthalene being regarded as a true benzene derivative in which the reduced nucleus functions as an aliphatic side chain. These formulas also offer an easy explanation as to why the reduction of naphthalene and its derivatives takes place in stages which show a marked difference from each other. Bamberger developed analogous formulas for quinoline, anthracene, and phenanthrene.

The researches of Ciamician and Angeli on pyrrol and its derivatives had in the meantime become generally known. Although this substance



contains an imido group it shows no basic properties, and even resembles phenol in its weak acidity. When reduced to dihydro-

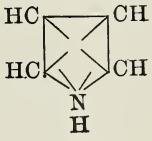
and tetrahydro-pyrrol, however, it suffers an abrupt change from acidic to strongly basic properties:



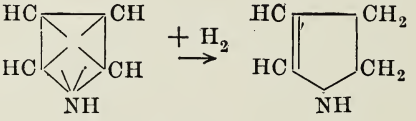
I II III

The formulas which are represented above do not explain the abrupt and abnormal change in properties observed in the transition from I to II as compared with the gradual and normal change in properties in the transition from II to III.

In order to explain these relationships better, Bamberger developed the following formula for pyrrol:



in which he assumes the presence of pentavalent nitrogen and also a system of six latent valencies similar in character to those present in benzene. The addition of hydrogen may be supposed to destroy the equilibrium of this system, and this is accompanied by a radical rearrangement of the molecule:



During this transformation nitrogen passes from the pentavalent to the trivalent condition, while at the same time an unsaturated double bond is established between two of the four carbon atoms. The abrupt change in the properties of the substance during the process of reduction is in this way readily accounted for.

Analogous formulas were soon evolved for indol, thiophene, furane and other similar compounds. It was not possible, however, to attach any lasting significance to the new formulas, and they were

finally abandoned, following criticism by Ciamician and Zanetti,[1] Markwald,[2] and others. The phenomena themselves remained unexplained, and continued to demand other and more adequate interpretations to replace those which had been rejected.

To summarize briefly, it may be said that the various investigations which have just been reviewed led to the conclusion that, while ring compounds of the benzene type are undoubtedly unsaturated, this characteristic is not so pronounced or so definite as in the case of unsaturated compounds of the paraffine series. The gradation in properties of unsaturated aromatic and aliphatic bodies undoubtedly bears some relation to the presence of conjugate double linkages in the molecule, but there seems to be no way of expressing these relationships in terms of the present structural formulas.

As a result of work along these lines a very keen interest was developed in regard to the relation of unsaturation to various physical properties. Researches were undertaken with a view to determining the influence of double bonds upon molecular volume, electrolytic conductivity, and, even more particularly, upon molecular refraction and dispersion. Developments in these fields of research will be referred to again later in this text. Still more recently, investigation has concerned itself with the effect of unsaturation upon other physico-chemical properties, such as dielectric constant, absorption spectrum, etc. In 1897 F. Henrich pointed out that the so-called negative character of certain groups of atoms was really conditioned by their unsaturation. He called attention to the fact that tautomeric as well as other types of rearrangements seem to depend upon the activity of unsaturated atoms or groups, and that recent speculation in regard to the relation between color (fluorescence, etc.) and chemical constitution is based upon a consideration of the properties of doubly bound atoms.

In general, the study of unsaturated compounds has opened up an almost infinite number of new problems, and has done much toward keeping theoretical speculation free from purely formal and inelastic conceptions, such as in the past have so often hindered the forward movement of science. Progress in chemistry at the present time is largely due to an appreciation of the fact that affinity does not operate exclusively as sharply defined units (valencies) but is capable of almost infinite variation. It is supposed that in the different types of simple combination residues of affinity are frequently left free, and that these may be relatively great or small, depending upon a variety of

[1] Ber., **24**, 2122 (1891); **26**, 1711 (1893).

[2] Annalen der Chemie, **274**, 331 (1893); **279**, 1 (1894).

conditions, but must in all cases play a quite definite rôle in determining the properties and the reactivity of the resulting compound. Certain theories, which have been of importance in the historical development of the conception of residual affinity must now be considered.

CHAPTER IV

JOHANNES THIELE'S THEORY OF PARTIAL VALENCIES

The idea that chemical action is due to attractive forces (valencies) operating between atoms came to be more and more generally accepted after the middle of the last century. This led to the deduction that where free valencies were known to exist chemical activity was to be expected, and conversely, that chemical activity indicated the presence of free valencies. The importance of the latter was overlooked by organic chemists partly because of the character of the chemical formulas which were then in use. While Kekulé had originally assumed that free valencies were present in unsaturated compounds, the fact that these were always observed to occur in pairs and that all attempts to prepare methylene $=CH_2$ resulted in the formation of ethylene, $CH_2{=}CH_2$, led to the assumption that the valencies, which were set free in the formation of unsaturated compounds, mutually saturated each other, thus giving rise to double and triple bonds between atoms. The formulas which were employed to express these ideas, could, however, be construed to mean something quite different from that for which they were intended. In the case of $CH_3{-}CH_3$, $CH_2{=}CH_2$, and $CH{\equiv}CH$, for example, the mere symbols suggest a greater stability for ethylene and acetylene than for methane, and this is, of course, directly contradictory to the facts. The first rational explanation of the gradually decreasing stability observed in compounds containing double and triple bonds was offered by A. v. Baeyer[1] in his so-called "tension theory" and was based upon van't Hoff's hypothesis in regard to the distribution in space of the four valencies of carbon. Other attempts to interpret the phenomena of unsaturation were advanced by von Wunderlich,[2] Victor Meyer and P. Jacobson[3] and others, and were in general agreement with that of Baeyer.

In 1899 Thiele[4] pointed out that while it was possible to explain the behavior of substances possessing a single pair of double or triple

[1] Ber., **18**, 2277 (1885).
[2] Konfiguration organischer Moleküle, Wurzburg, 1886.
[3] Lehrbuch der Organischen Chemie, Vol. I.
[4] Annalen der Chemie, **306**, 87 (1899).

bonds by means of the theories which have just been referred to, it was impossible to interpret in the same manner the properties of substances possessing two pairs of adjacent double bonds. Thus, for example, R. Fittig [1] has shown, as the result of a series of investigations in regard to the constitution of piperic acid, that this substance,

$$CH_2(O_2)C_6H_3CH : CHCH : CHCOOH$$

always gives as its normal reduction product α-hydropiperic acid

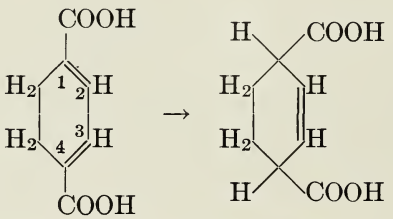
$$CH_2(O_2)C_6H_3CH_2CH : CHCH_2COOH$$

and that, therefore, hydrogen always adds primarily in the 1–4, never in the 1–2 or 3–4 positions. The transformation to β-hydropiperic acid,

$$CH_2(O_2)C_6H_3CH_2CH_2CH : CHCOOH$$

is brought about only as the result of the action of sodium hydroxide.

Similar observations were made by Baeyer [2] in connection with the reduction of terephthalic acid. Thus in the case of Δ^{1-3}-dihydroterephthalic acid, hydrogen adds in the 1–4 and not in the 1–2 or 3–4 positions, with formation of a new double bond between the 2–3 positions of the ring.



Realizing the importance of this discovery Baeyer, in co-operation with Rupe,[3] extended his research into the aliphatic series and studied the behavior of the atomic grouping

$$—CH{=}CH \cdot CH{=}CH—$$

in muconic acid,

$$\underset{1}{HOOC} \cdot \underset{2}{CH} : \underset{3}{CH} \cdot \underset{4}{CH} : CHCOOH$$

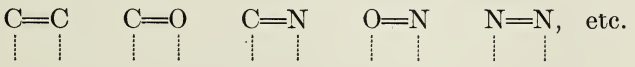
The results of this investigation also show that addition both of hydrogen and of halogen takes place in the 1–4 and not in the 1–2 or

[1] Annalen der Chemie, **152**, 47; **172**, 158; **216**, 171; **227**, 46 (1888).
[2] Annalen der Chemie, **251**, 271 (1889).
[3] Annalen der Chemie, **256**, 1 (1890).

3–4 positions. Thiele contributed still other data to those furnished by Fittig, Baeyer and Rupe, and in every case the evidence seemed to point to the fact that addition to unsaturated systems possessing conjugate double bonds usually takes place in the 1–4 positions.

Thiele's Theory of Partial Valencies attempts to explain these important facts on the basis of previous assumptions in regard to the chemical nature of the carbon atom.[1] If a substance containing doubly bound carbon atoms, as for example ethylene, is brought in contact with one of the halogens, a very vigorous addition reaction takes place even at ordinary temperatures, with the result that two atoms of halogen combine respectively with the two doubly bound carbon atoms. These carbon atoms must be regarded as very reactive, and, according to Thiele, the reason for this is to be found in the fact that they possess free valencies. Such *free valencies* are of a particular type, however, and must not be confused with the ordinary conception of *free unit valencies*. In the case of ethylene, for example, the two unsaturated carbon atoms may be imagined as joined together by means of four valencies which have united to form a double bond; but in this union all four valencies are not mutually and completely saturated, since in the case of the second pair only a fraction of each unit of affinity is exercised in holding the two carbon atoms together, while a residue of affinity is left free. To this residue of free affinity Thiele gives the name " Partial Valency," and he represents it graphically in a chemical formula by means of a dotted line.

This idea was developed still further by Thiele and was applied not only to all doubly bound carbon atoms but also to other unsaturated atoms in organic combinations, the symbols for which may be written in the following way:



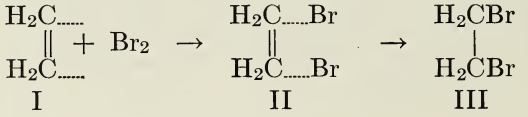
The relative strength of the partial valencies may, of course, be assumed to be different in different cases. Such formulas show why unsaturated groups of atoms are reactive, but they do more in that they afford a basis for the development of an entirely new point of view. To understand this fully it will be necessary to consider in detail Thiele's theory of partial valency.

As has already been pointed out, chemists at this time had abandoned the conception of free valencies and had assumed the presence

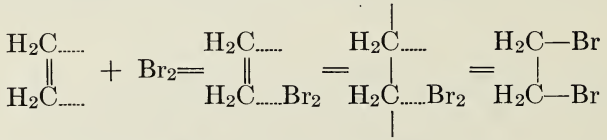
[1] Annalen der Chemie, **306**, 87 (1899); **308**, 333 (1899).

of multiple forms of union in unsaturated compounds. In 1892 Nef [1] again brought forward the idea of free valencies and at the same time Armstrong [2] attempted to explain the cause of certain chemical reactions on the assumption of so-called residual affinities. Both theories vary from that of Thiele, however, since the latter assumes that in unsaturated compounds the atoms are actually joined together by means of double or triple bonds, but possess in addition a certain residue of free affinity. Thiele's conception finds support in the thermochemical investigations of J. Thomson,[3] who shows that the heat of formation of ethylene is less than should be expected if two simple pairs of carbon linkages are present in the molecule: "This would signify that in the formation of an unsaturated compound of this type, not all of the energy, belonging to the four units of valency, is exercised in holding the two carbon atoms together or that, in other words, they still possess residues of free affinity or partial valencies."

In all additions to ethylene the reacting atoms or groups of atoms are supposed to attach themselves by satisfying the residues of free affinity present in the molecule but, according to Thiele, this is followed immediately by the ruption of one of the double bonds between the carbon atoms, and the final arrangement is one in which the adding atoms or groups completely saturate respectively each of two unit valencies of the carbon atoms. In the case of bromine, for example, the various stages involved in the process of addition to ethylene may be represented in the following manner:



Reich [4] formulates this reaction as follows:



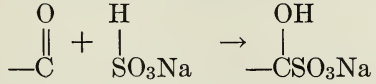
[1] Annalen der Chemie, **270**, 267 (1892); **280**, 291 (1894); **287**, 265; **298**, 202; **309**, 264. Also "The Fundamental Conceptions Underlying the Chemistry of the Element Carbon," see Chapter XIV.

[2] Jour. Chem. Soc., **51**, 264 (1887).

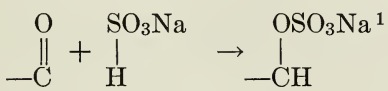
[3] Zeitschr. physikal. Chemie, **1**, 369 (1887).

[4] Such intermediate products have never as yet been isolated. Annalen der Chemie, **306**, 105 (1911); **319**, 129 (1912). Also compare Reich, Jour. prakt. Chemie **90**, 177 (1914) and Reddelien, ibid., **91**, 219.

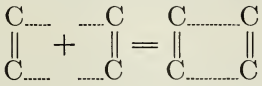
Since the different elements have different attractions for each other, it follows that addition reactions will be greatly influenced by the nature of the atoms involved. Nitrogen, for example, has only a very slight affinity for halogen, and, therefore, N=N adds halogen only with difficulty. Since hydrogen has a greater affinity for oxygen than for carbon, while the reverse is true in the case of the group $-SO_3Na$, it follows that the addition of sodium bisulphite to ketone and aldehyde groupings takes place according to the scheme:



and not according to the equation below:



This conception of free valency suggests the possibility that under certain conditions compounds may exist in which atomic stability within the molecule depends in part upon the exercise of partial valencies. The primary product (II) resulting from the addition of bromine to ethylene would belong to this class of bodies, as would similarly the polymerization products of the ethylene hydrocarbons:

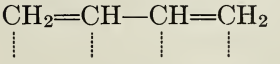


Such complex molecules would be more saturated in character than the simple molecules from which thay are derived, but would readily break down into their components. Metastyrol and other polymerization products showing saturated properties may possibly be regarded as compounds of this type.[2]

When two pairs of doubly bound carbon atoms occupy adjacent positions in the molecule they are said to form a "conjugate system." The simplest type of such a system may be represented by

$$E{=}E{-}E{=}E$$

where E equals any element. If the particular element happens to be carbon, for example, it follows according to Thiele's theory that each atom present in the chain possesses a partial valency:



[1] Annalen der Chemie, **306**, 92 (1899).

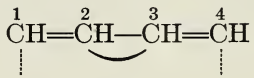
[2] Compare Willstätter, Ber., **41**, 1464 (1908).

In this case the reduction of butylene[1] (butadiene) should result in the simultaneous addition of four hydrogen atoms to each of the four carbon atoms. Actual observation has shown, however, that only two hydrogen atoms add to the hydrocarbon and that they attach themselves not to two adjoining carbon atoms such as 1–2 or 3–4, but to the end carbon atoms in the positions 1 and 4 forming *sym*-dimethylethylene.

$$CH_2 : CH \cdot CH : CH_2 + H_2 \rightarrow CH_3CH : CHCH_3$$

The addition of bromine takes place in the same way, and a symmetrical unsaturated dibromide is formed, $BrCH_2CH : CH \cdot CH_2Br$.

This remarkable behavior has been observed in the case of innumerable compounds possessing analogous atomic groupings and may be explained by supposing that in systems of this type the partial valencies on the atoms 2 and 3 mutually saturate each other, combining to give a new kind of double bond between the respective atoms. Thiele calls this form of combination an "inactive double bond." The system of atoms as a whole receives the name of a conjugated system and may be represented graphically in the following way:

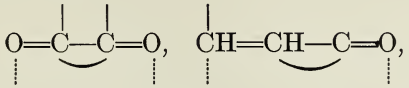


If the above scheme correctly expresses the relationships of the atoms in compounds which contain two adjacent pairs of doubly bound carbon atoms, it is easy to see why addition takes place primarily in the 1–4 positions, for the adding atoms or groups will naturally attach themselves so as to neutralize the free residual affinities of the end carbon atoms. Since the adding atoms will themselves require more affinity for saturation than is afforded by the partial valencies, addition will be immediately followed by a rupture of the double bonds joining the pairs of atoms 1–2 and 3–4. The free affinities on 2 and 3 will then combine to form a double bond which will replace the inactive single bond between the central atoms. In this way the formation of symmetrical addition products may be readily accounted for in all cases.

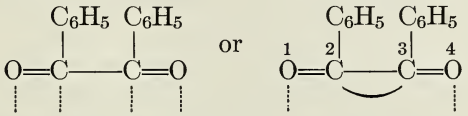
Substances which possess conjugated double linkages are more highly saturated than substances which possess two separate pairs of double bonds, and should, therefore, show lower heats of combustion. In general this may be said to be actually the case.

[1] Annalen der Chemie, **308**, 333 (1899).

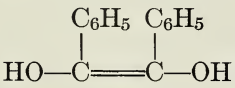
Conjugated systems may be made up of heterogeneous pairs of atoms, as, for example,



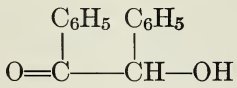
and the question naturally arises as to whether the same general rules for addition apply in all cases. This question may be answered by considering the chemistry of benzil, for example, to which either one or the other of the following structural formulas may be assigned:



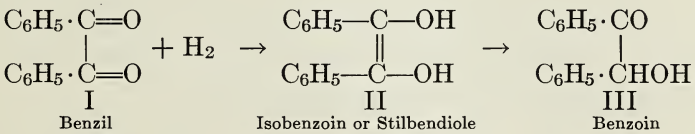
If hydrogen adds in the 1–4 position, dihydroxystilbene should be formed



but such is not the case since benzil on reduction gives a ketone-alcohol combination, i.e.,

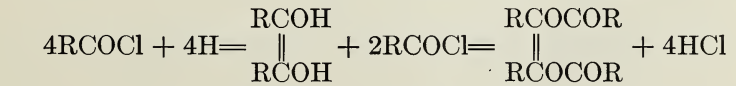


At first sight this result would seem to indicate 3–4 addition, but such is not necessarily the case since it is possible to assume that the unsaturated alcohol, dihydroxystilbene, is formed as a primary product in the reduction and then immediately rearranges to give the stable combination benzoin:



In fact, it has been observed frequently that attempts to prepare the unsaturated atomic grouping C(OH)=C result in the formation of a ketone linking O=C—CH.

In his interesting research on isobenzil, H. Klinger[1] has shown that acid chlorides are reduced according to the following equation:



[1] Ber., **24**, 1268, 1271 (1890); **31**, 1217 (**1898**).

In an effort to prove that dihydroxystilbene is actually formed as an intermediate product in the reduction of benzil, Thiele attempted to stop the reaction at this stage, and he succeeded in doing this by the ingenious device of carrying out the reduction in the presence of a protective solvent, namely, acetic anhydride and concentrated sulphuric acid. In this way the hydroxyl groups were acetylated as rapidly as they were formed and before sufficient time had elapsed to allow for the rearrangement of the dihydroxystilbene into benzoin. As products of the reduction Thiele obtained two diacetates which were found to be stereoisomers and which were different from the diacetate obtained by the acetylization of benzoin. They were regarded by Thiele as the diacetyl derivatives of dihydroxystilbene, and as, in general, offering valuable confirmation of his theory.[1]

In atomic groupings such as CH=CH·CH=CH and O=C·C=O, the adjacent pairs of doubly bound carbon atoms are identical in character, and the partial valencies on the atoms 2 and 3 are therefore of equal strength, and should exactly neutralize each other to form an inactive double bond. The case is somewhat different when the conjugated system is made up of unequal pairs of doubly bound atoms as, for example, in the grouping $\underset{1}{CH}=\underset{2}{CH}\cdot\underset{3}{CH}=\underset{4}{O}$. Here it is necessary to suppose that the partial valencies of CH=CH are of different relative strength from those of C=O, and that therefore an inactive double bond between 2 and 3 is impossible. In an exchange of affinity between these carbon atoms either one or the other must be left with a residue of free affinity, or in other words, with a partial valency of a lower order.

Such a mixed system of conjugate double linkages may or may not react as a unit.[2] It is present in unsaturated aldehydes and ketones, and its behavior on reduction may be considered in the case of benzylideneacetone. According to earlier views ready reduction of the carbonyl group in this substance was to be expected:

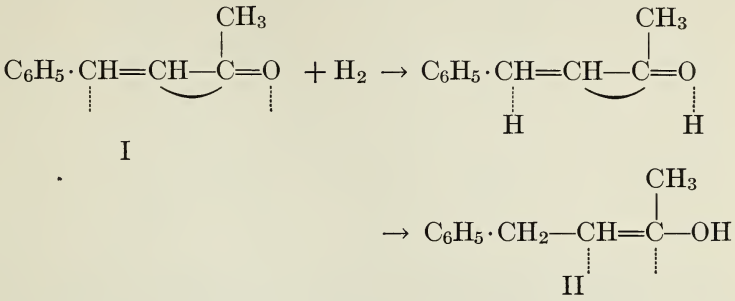
$$C_6H_5CH{=}CHC(CH_3){=}O + H_2 \rightarrow C_6H_5CH{=}CHCH(CH_3)OH$$

As a matter of fact this reaction does not take place, the reduction product being $C_6H_5CH_2CH_2COCH_3$. The formation of this sub-

[1] For other interpretations compare Werner, Chem. Zeitung, **1**, 4; also Erlenmeyer, Jr., Jour. prakt. Chemie, **65**, 351 (1902).

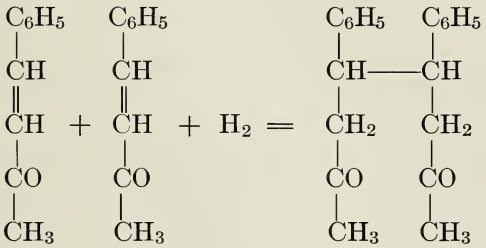
[2] For a detailed discussion in regard to the "Distribution of affinity in organic compounds" see Borsche, Annalen der Chemie, **375**, 147 (1910).

stance may be explained, however, in the terms of Thiele's theory, by supposing that the primary reaction is one of 1–4 addition:

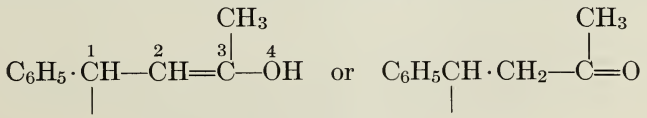


and that this is followed by the immediate rearrangement of the unstable *enol* combination into the corresponding tautomeric ketone, viz., benzylacetone $C_6H_5CH_2CH_2COCH_3$. The latter, being the more stable modification, forms the main product of the reaction. In this way it is easy to understand why the carbonyl group, which usually reduces so readily, fails in this case to give —CHOH.

Harries [1] has shown that the reduction of unsaturated ketones may readily take a course which involves the interaction of two molecules. Benzylideneacetone, for example, may react in the following way:

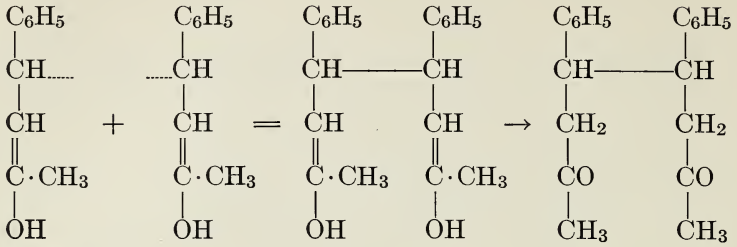


In such cases condensation always takes place in the β- and never in the α-position with respect to the carbonyl. While previous to this time there had seemed to be no good reason for this behavior it, too, may be readily explained in terms of Thiele's theory. For since hydrogen has a greater affinity for oxygen than for carbon, one atom of hydrogen might naturally add first to oxygen in the 4-position giving

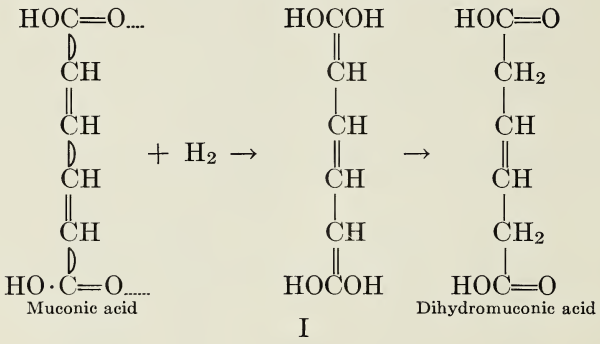


[1] Annalen der Chemie, **296**, 295 (1897).

and two such residues might then combine by the saturation of partial valencies in the 1-positions:

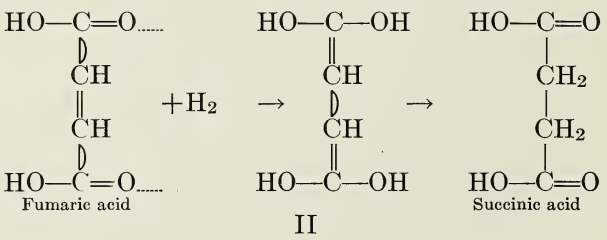


The reduction of unsaturated acids is also explained in an unusually plausible manner. Ease in reduction had been shown by Baeyer [1] to depend upon the proximity of the ethylene to the carbonyl groups, and this may be accounted for in the following way:



I

and again,



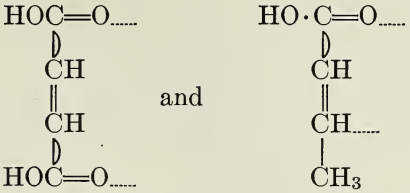
II

Intermediate products corresponding to I and II have not as yet been obtained, but this may be readily explained as due to instantaneous tautomeric rearrangements.

The crotonic acids are known to be much less readily reducible than fumaric and maleic acids. This difference in behavior would be

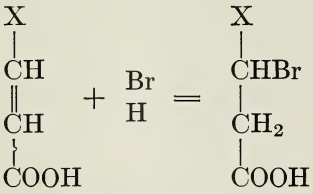
[1] Loc. cit.

difficult to explain on the assumption that in these reduction reactions hydrogen adds to the unsaturated ethylene linkages, but may be readily interpreted by means of Thiele's formulas for these substances, i.e.,

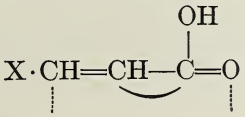


if the fact is borne in mind that hydrogen has a much greater affinity for oxygen than for carbon.

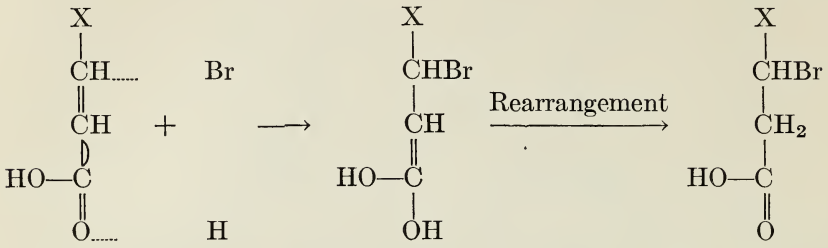
The addition of halogen to systems of conjugated double bonds takes place in much the same way as has been described in the case of hydrogen. A study of the addition of the halogen acids to α-, β-, unsaturated acids has shown that the halogen atom regularly assumes a β-position with reference to the carboxyl group of the acid, and the phenomenon has been represented by means of the following equation:



It was, however, impossible to explain this behavior in any rational way. The facts were simply accepted as an empirical law and all attempts to interpret them were dismissed dogmatically by saying: "halogen is repelled by carboxyl." The negative character of the two might be supposed to account for this, were it not that the NH_2 group, which is commonly regarded as positive in character and should therefore be attracted by carboxyl, also adds to unsaturated α-, β-acids in the β-position. Thus the positive or negative character of the adding atoms or groups of atoms does not seem to influence the reaction. Thiele's theory, on the other hand, offers a very plausible elucidation of the phenomena. In terms of this theory, free residual affinity exists in two positions in the acid molecule,



and in all additions involving hydrogen it may be assumed that preference will be given to the 4-position. Hydrobromic acid will therefore react according to the following scheme:



and the same general diagram may be used to explain additions involving H—Cl, H—I, H—OH, H—NH_2, acids, etc.

1–4 addition to conjugated systems is not, however, a rule which has no exceptions.[1] Thiele,[2] himself, has pointed out that double bonds, present in such systems, may at times react quite independently of one another. Such independent action may be expected when the adding atoms or groups possess a strong affinity for a particular pair of the atoms which are held together by double bonds. In the case of the complex C=C—C=O, for example, it may be anticipated that halogen will favor ethylene, and that HCN on the other hand will add preferably to the carbonyl group. Hydrogen alone adds almost exclusively in the 1–4 positions.[3] The halogens react very irregularly, as is shown from a consideration of the following facts: butadiene, $CH_2{=}CH{\cdot}CH{=}CH_2$, adds bromine in the 1–4 positions, giving $CH_2BrCH{=}CHCH_2Br$ as the main product of the reaction, although small quantities of the isomer $CH_2BrCHBrCH{=}CH_2$ are also formed; phenylbutadiene, $C_6H_5CH{=}CHCH{=}CH_2$, on the other hand, adds bromine almost exclusively in the 3–4 positions while diphenylbutadiene, $C_6H_5CH{=}CHCH{=}CHC_6H_5$, gives a 96 per cent yield of the 3–4 dibrom addition product and it is even questionable whether 1–4 addition takes place at all in this case.

[1] Erlenmeyer, Annalen der Chemie, **316**, 43 (1901); Vorländer, Annalen der Chemie, 320, 73 (1902); **345**, 206 (1906); Michael, Jour. prakt. Chemie, **60**, 467 (1899); **68**, 503, 512 (1903); **75**, 119; Thiele and Häckel, Annalen der Chemie, **325**, 6 (1902); Hinrichsen, Zeitschr. physikal. Chemie, **39**, 308 (1902); Ber., **37**, 1121 (1904); Annalen der Chemie, **336**, 168 (1904); Flürscheim, Jour. prakt. Chemie, **71**, 503 (1905); Bauer, Jour. prakt. Chemie, **72**, 206 (1905); Bamberger, Ber., **40**, 2239 (1907); Kohler, Chem. Centralbl., 1908, I, 226; Meyer and Jacobson's Lehrbuch der organischen Chemie, Vol. I, 795 (2d edition).

[2] Annalen der Chemie, **306**, 106 (1899).

[3] Ber. **42**, 2872 (1909).

F. Straus [1] sums up the situation in regard to the addition of bromine to conjugate systems of ethylene linkages when he says, " 1–4 addition may take place, but it is not the rule. No single instance has as yet been observed, at least in connection with open chain compounds, where 1–4 addition takes place exclusively."

Although, as Wieland [2] has pointed out, nitrogen dioxide usually resembles halogen in addition reactions, in the case of diphenylbutadiene it reacts quite differently, adding in the 1–4 positions to give 1–4-dinitrodiphenylbutylene,

$$C_6H_5CH(NO_2)CH{=}CH{-}CH(NO_2)C_6H_5$$

Hinrichsen [3] attempts to explain this difference in behavior by supposing that the mutual repulsion of nitro groups is considerably greater than that of bromine atoms. Thus while the bromine molecule dissociates only at high temperatures, the dissociation of N_2O_4 into $2NO_2$ takes place readily and at relatively low temperatures. The relationships involved in additions to conjugated systems are undoubtedly very complicated and, in the words of Hinrichsen, are " conditioned not only by kinetic and stereochemical influences, but quite as much by the purely qualitative affinities operating between the adding atoms themselves, or between them, on the one hand, and the atoms or groups of atoms present in the unsaturated molecule." According to this investigator, two types of reaction may be differentiated:

I. Where the components of the adding molecules are electrochemically different in character. The components in this case exercise an attraction for each other and will attach themselves to positions as close together as possible. This condition favors 1–2 addition and is illustrated by the following equation: [4]

$$C_6H_5CH{=}CH{-}CH{=}C(COOC_2H_5)_2 + HCN \rightarrow C_6H_5CH{=}CH\cdot\underset{\displaystyle CN}{\underset{|}{CH}}\cdot CH(COOC_2H_5)_2$$

Independent additions are naturally more frequent in the case of heterogeneous systems. Thus, in the action of HCN upon cinnamic aldehyde, the carbonyl group alone is affected,

$$C_6H_5CH{=}CHCHO + HCN \rightarrow C_6H_5CH{=}CHCHOHCN$$ [5]

[1] Ber., **42**, 2872 (1909).
[2] Annalen der Chemie, **360**, 306 (1908).
[3] Chem. Zeitung (1909), 1098.
[4] Compare also Ber., **44**, 2974 (1911).
[5] Annalen der Chemie, 306.

and this is also true in the addition of methyl magnesium iodide.[1] Cinnamoyl formic acid reduces to give primarily phenyl α-hydroxyisocrotonic acid:[2]

$$C_6H_5CH{=}CHCO\cdot COOH + H_2 \rightarrow C_6H_5CH{=}CHCHOH\cdot COOH$$

On the other hand, Harries[3] and his students have shown that in the reduction of unsaturated ketones of the general formula $R_2C{=}CH{-}COR$, the ethylene linkage is the one which is primarily attacked while the carbonyl is affected only secondarily. The same is true in additions of hydroxylamine.

According to Vorländer[4] the ethylene linkage alone is involved in reactions between sodium malonic ester and derivatives of cinnamic acid:

$$C_6H_5\cdot CH{=}CH{-}\overset{\displaystyle X}{\overset{|}{C}}{=}O + NaCH(COOC_2H_5)_2 = C_6H_5\cdot \overset{\displaystyle CH(COOC_2H_5)_2}{\overset{|}{CH}}{-}\overset{\displaystyle Na\ X}{\overset{|\quad|}{CH}}{-}C{=}O$$

Even in the case of two conjugated ethylene linkages, 1–2 or 3–4 addition frequently takes place. Thus, according to Hinrichsen,[5] bromine adds to cinnamylidene derivatives according to the equation:

$$C_6H_5\cdot CH{=}CH{-}CH{=}C\begin{matrix}\diagup CN(C_6H_5,\text{ or } COOC_2H_5)\\ \diagdown COOC_2H_5\end{matrix} + Br_2$$

$$= C_6H_5\cdot \underset{Br}{CH}{-}\underset{Br}{CH}{-}CH{=}C\begin{matrix}\diagup CN(C_6H_5,\text{ or } COOC_2H_5)\\ \diagdown COOC_2H_5\end{matrix}$$

Phenyl, or carbethoxy $COOC_2H_5$, may be substituted for cyanogen without affecting the course of this reaction.

The following substances add to double unions in a manner analogous to that described in the case of hydrogen cyanide, viz.,—*p*-toluene sulphinic acid, $C_7H_7SO_2H$; acid potassium sulphite, $HKSO_3$; ammonia, NH_3; the sodium salt of malonic ester, $NaCH(COOR)_2$; sodium ethylate, $NaOC_2H_5$; benzyl mercaptan, $C_6H_5CH_2SH$; and hydroxylamine NH_2OH.

II. Where the components of the adding molecules are electrochemically similar in character either one of two things may happen:

[1] Ber., **36**, 2529 (1903).
[2] Ber., **35**, 2649 (1902).
[3] Ber., **28**, 150 (1895); **29**, 375, 380; **30**, 230 (1897); Posner, **36**, 4305 (1903), etc.
[4] Annalen der Chemie, **320**, 60 (1902); Ber., **36**, 172, 2339 (1903).
[5] Annalen der Chemie, **336**, 323 (1904).

(*a*) The mutual repulsion of the two parts of the adding molecule may be reinforced by the character of the components of the unsaturated molecule. This is illustrated in the addition of N_2O_4 to diphenylbutadiene, to which reference has previously been made. Another example is the addition of hydrogen to phenylcinnamylacrylic acid:

$$C_6H_5\cdot CH{=}CH{-}CH{=}C\begin{cases}C_6H_5\\COOH\end{cases} + H_2$$

$$= C_6H_5\cdot \underset{\dot{H}}{CH}{-}CH{=}CH{-}\underset{\dot{H}}{C}\begin{cases}C_6H_5\\COOH\end{cases}$$

In other words, in reactions involving an addition of hydrogen, this element tends to attach itself to the carbon atoms holding negative groups (C_6H_5, COOH, etc.).

(*b*) The two parts of the adding molecule may be definitely attracted by atoms or groups of atoms present in the unsaturated molecule. Such a condition may be supposed to account for the addition of bromine to cinnamylidene malonic ester, and also hydrogen to dibenzalpropionic acid. In the case of the malonic ester 3-4 addition is impossible since the two negative carbethoxy groups actively repel the bromine and 1-2 addition takes place exclusively:

$$C_6H_5\underset{1}{CH}{=}\underset{2}{CH}{-}\underset{3}{CH}{=}\underset{4}{C}(COOR)_2 + Br_2$$

$$= C_6H_5{-}CH\ Br\cdot CH\ Br\cdot CH{=}C(COOR)_2$$

The addition of hydrogen to dibenzalpropionic acid is expressed as follows:

$$C_6H_5\cdot CH{=}CH{-}\underset{\substack{|\\COOH}}{C}{=}CH{-}C_6H_5 + H_2$$

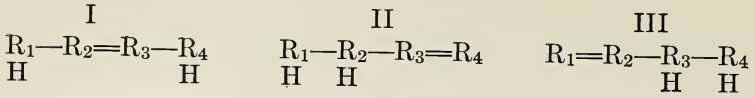
$$= C_6H_5\cdot CH{=}CH{-}\underset{\substack{\diagup\ \diagdown\\H\quad COOH}}{C}{-}CH_2{-}C_6H_5$$

Here again, in reactions involving an addition of hydrogen, this element tends to join with the carbon atoms holding negative groups (C_6H_5, COOH, etc.).

Erlenmeyer, Jr.,[1] even goes so far as to say that it is impossible to predict how hydrogen and bromine will add to conjugate systems

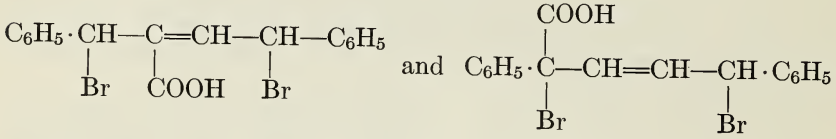
[1] Jour. Prakt. Chemie, **65**, 354 (1902).

of the type $R_1{=}R_2{-}R_3{=}R_4$. The reaction may take place according to him in any one of three ways, viz.:

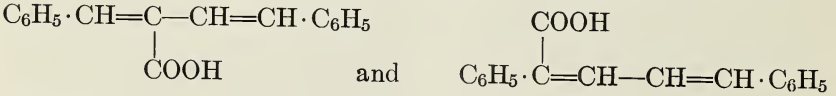


and the result can be determined only by experiment.

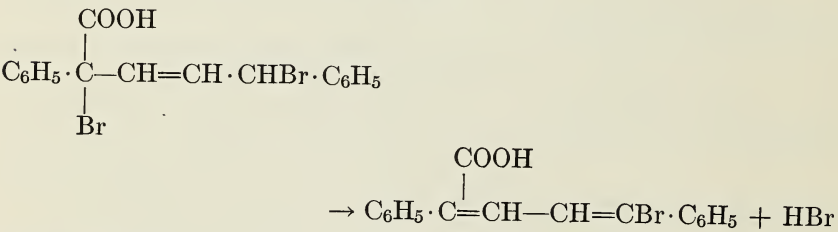
If the conditions favoring addition reactions are reversed, it should follow that atoms may be split off from these various addition products with the result that the original system, $R_1{=}R_2{-}R_3{=}R_4$ is formed. Such a conclusion has been demonstrated experimentally. Thus when Thiele reduced the dibromides,



by the action of zinc dust and acetic acid, he obtained the acids,

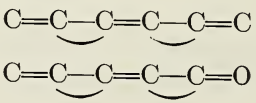


Indeed he was even able to split off hydrobromic acid from the 1–4 positions. Thus the following change:



was brought about when the dibromide was treated with potash.[1]

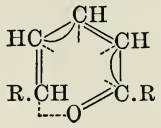
Conjugate systems consisting of three pairs of doubly-bound atoms may now be considered, viz.,



A study of atomic groupings of this type shows at once that the distribution of affinity is such that partial valencies appear only on

[1] Annalen der Chemie, **306**, 109; **316**, 46–49; **323**, 217; Ber., **40**, 2239 (1908).

atoms which are located at the ends of the chain. The magnitude of the residual free affinity in these positions may be assumed to be relatively great, but need not manifest itself in increased chemical reactivity, since it is quite possible that the partial valencies on terminal atoms may mutually saturate each other according to the following scheme:



Such an arrangement would obviously tend to decrease rather than increase the chemical reactivity of the substance.

It should be noted at this point that groups such as $-CH_2Cl$, $-CHCl_2$, $-CCl_3$, or in general $\rangle CCl$, may, according to H. Finkelstein,[1] be regarded as unsaturated and, therefore, capable of forming addition products. Thus the reduction of a halide is comparable to the reduction of a ketone to its alcohol.

$$R_2C{=}O + H_2 = \underset{H\ H}{R_2C{=}O} \rightarrow R_2CH{-}OH$$

$$R_3C{-}Cl + H_2 = \underset{H\ H}{R_3C{-}Cl} \rightarrow R_3CH + HCl$$

The interaction of silver hydroxide and magnesium with halides is expressed as follows:

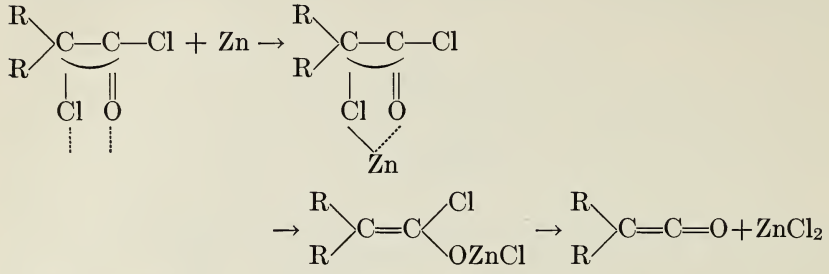
$$R_3C{-}Cl + AgOH = \underset{OH\ Ag}{R_3C{-}Cl} \rightarrow R_3COH + AgCl$$

$$R_3C{-}Cl + Mg = \underset{Mg}{R_3C{-}Cl} \rightarrow R_3C{-}MgCl.$$

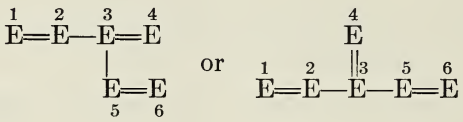
If such unsaturated halide groups occupy positions in the molecule which are adjacent to other unsaturated groups, conjugate systems may arise. Speculation along this line has led, in a number of instances, to very plausib e interpretations of difficult phenomena. Thus, for example, acid chlorides do not react spontaneously with metals like zinc, while the corresponding halogen substitution products under the

[1] " Verhandl. d.d. Naturforscherversammlung," 1911, II, 176 and following.

same conditions readily give ketones. The cause of the increased chemical activity in the second case is indicated by the following formulas which show the addition of zinc to a conjugate system of this type:



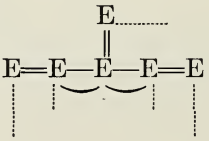
If three or more conjugate double bonds are arranged not in a straight but in a branched chain, as for example,



they form what Thiele calls systems of " Crossed Double Bonds "; and may be regarded as made up respectively of two separate systems namely:

1–2–3–4 and 4–3–5–6

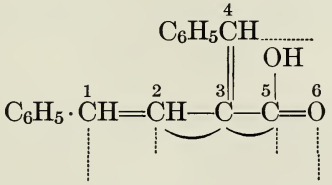
If E represents atoms of the same element it follows that the partial valency of 3 will exactly equal that of 1, 2, 4, 5 or 6 respectively, and if this is the case, it obviously cannot neutralize completely the free affinity of both 2 and 5. The atoms 2 and 5 must, therefore, continue to carry a certain residue of free affinity (equal to one-half of the partial valency). The distribution of free energy, therefore, in such a system may be expressed by means of the following diagram:



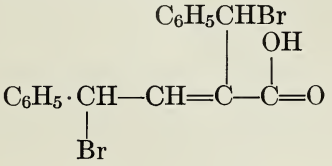
If the atoms are not all exactly alike, the relative values of the residual affinities will, of course, be different from that which is represented above.

It should be noted at once that not only is the relative free affinity of the terminal atoms greater than in the case of simple conjugate systems, but the total quantity of free affinity present in the molecule is also greater. The latter fact is demonstrated in a most convincing way by a study of the physical constants of this class of substances, but a detailed discussion of this important aspect of the subject must be reserved for another chapter.

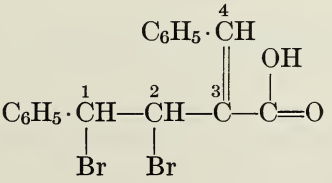
The chemical reactions of such a system may be considered in connection with dibenzalpropionic acid,[1] which serves as a convenient illustration:



The two conjugate systems which are present in the molecule, are respectively 1–2–3–4– and 4–3–5–6. Which of these two systems will take part in a given reaction will depend largely upon the nature of the reagent employed. Thus bromine adds to the system 1–2–3–4 since its affinity for carbon is greater than its affinity for oxygen. The main product of the reaction in this case is the dibromide,



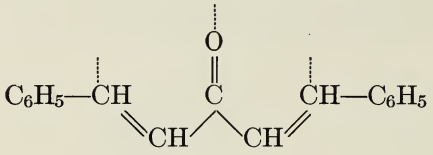
showing 1–4 addition; but the isomeric dibromide,



representing 1–2 addition, is also formed as a secondary product. Hydrogen and hydrobromic acid, on the other hand, add to the system 4–3–5–6, since the affinity of hydrogen is greater for oxygen than for carbon. In the case of hydrogen the reaction results in the formation of $C_6H_5CH{=}CH{-}CH(COOH)\cdot CH_2C_6H_5$.

[1] For other illustrations see Annalen der Chemie, **306**, 115.

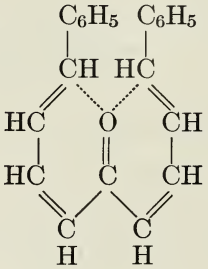
The application of Thiele's theory to the chemistry of naphthalene and related ring compounds is very interesting and will be considered briefly. It has already been noted in connection with straight chain conjugate systems that the partial valencies on the terminal atoms may mutually saturate each other if brought into juxtaposition, and strictly analogous conditions may arise in the case of systems of crossed double bonds. It has been observed, for example, that while dibenzalacetone,



readily adds ethylacetoacetate in the presence of pyridine as a condensing agent, dicinnamalacetone,

$$C_6H_5CH{=}CH\cdot CH{=}CHCOCH{=}CH\cdot CH{=}CHC_6H_5$$

does not. The inactivity of the latter compound is interpreted by Borsche [1] as due to the intramolecular saturation of the partial valencies on the terminal carbon atoms and may be represented diagrammatically in the following manner:



It has also been observed that dianisalacetone,

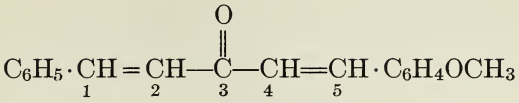
$$H_3CO\cdot C_6H_4\cdot \underset{1}{CH}{=}\underset{2}{CH}{-}\underset{3}{C}{-}\underset{4}{CH}{=}\underset{5}{CH}\cdot C_6H_4\cdot OCH_3 \quad (O \text{ on } C_3)$$

and tetramethyl-*p*-*p*′-diamidodibenzalacetone:

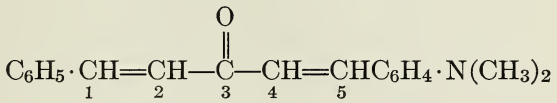
$$(CH_3)_2N\cdot C_6H_4\cdot \underset{1}{CH}{=}\underset{2}{CH}{-}\underset{3}{C}{-}\underset{4}{CH}{=}\underset{5}{CH}\cdot C_6H_4\cdot N(CH_3)_2 \quad (O \text{ on } C_3)$$

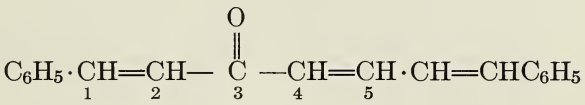
[1] Annalen der Chemie, **375**, 152 (1910).

fail to react with ethyl acetoacetate, while compounds like benzalanisalacetone,

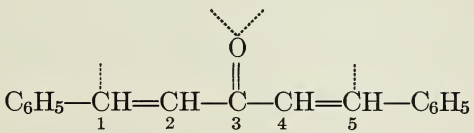


p-dimethylamidodibenzalacetone and benzalcinnamalacetone

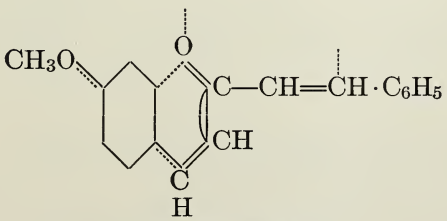




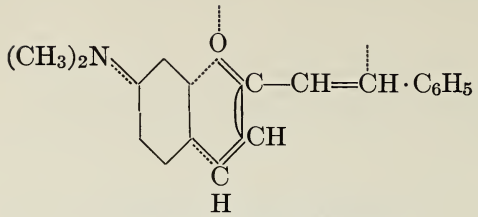
which contain at least one $CH=CHC_6H_5$ group, still react with this β-ketone ester, although much less readily than dibenzalacetone itself. Borsche explains the interference offered by the substitution of the $-C_6H_4OCH_3$ and the $-C_6H_4\cdot N(CH_3)_2$ groups by supposing that the partial valencies, which are present on the oxygen and nitrogen atoms of these radicals, are saturated by those which are present on the carbon atoms 1 and 5. The free affinity on the oxygen of the carbonyl group is simultaneously decreased by the influence of the CH_3O and $(CH_3)_2N$ groups. These relationships may be expressed by means of the following formulas which explain themselves:



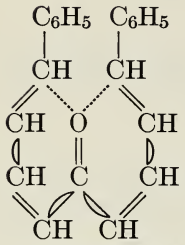
Dibenzalacetone



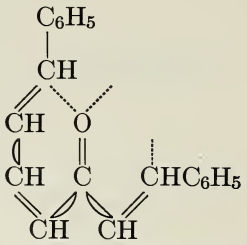
Benzalanisalacetone



Dimethyl-*p*-amidodibenzalacetone



Dicinnamalacetone



Benzalcinnamalacetone

The relative reactivity of unsaturated linkages in different substances seems to depend upon the character of the substituents which are in union with the doubly bound atoms, although as yet only a few quantitative experiments have been made to determine the exact extent of such influences. An investigation of this nature has, however, recently been undertaken by H. Staudinger [1] and N. Kon in connection with their interesting researches on ketenes. Diphenylketene,[2] $(C_6H_5)_2C{=}C{=}O$, was treated at 131° with various aldehydes and ketones of the general formula, $C_6H_5CH : CHCOR$,[3] when it was observed that the carbonyl group adds in every case directly to the ketene. This change is immediately followed by the decomposition of the addition product with the evolution of carbon dioxide and the formation of an ethylene derivative. The complete reaction is expressed by the following equation:

$$(C_6H_5)_2C{=}C{=}O + R_2C{=}O^4 = \begin{array}{l} (C_6H_5)_2C{-}C{=}O \\ \qquad\qquad\quad | \qquad\quad | \\ \qquad\qquad R_2C{-}O \end{array}$$

$$\begin{array}{l} (C_6H_5)_2C{-}C{=}O \\ \qquad\quad | \qquad\quad | \\ \qquad R_2C{-}O \end{array} = \begin{array}{l} (C_6H_5)_2\cdot C \\ \qquad\qquad\quad \| \\ \qquad\qquad R_2C \end{array} + \begin{array}{l} C{=}O \\ \| \\ O \end{array}$$

[1] Annalen der Chemie, **384**, 38 (1911); **387**, 254 (1912).

[2] In the form of diphenylketene quinoline.

[3] Where R may be $CH{=}CHC_6H_5$, H, C_6H_5, CH_3, OCH_3, $N(C_6H_5)_2$.

[4] See Staudinger "Die Ketene," Stuttgart, Enke, 1912.

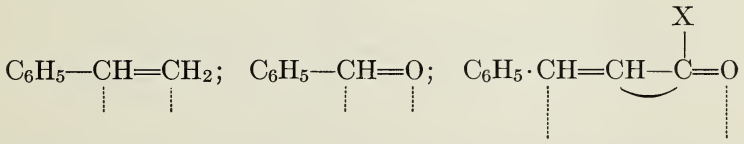
It is possible to study the relative reactivity of the carbonyl group in different compounds by observing the relative speed of this reaction. Although it is impossible to exclude side reactions entirely and so to obtain invariable constants, it is, nevertheless, possible to gauge the reactivity of the carbonyl group roughly from the quantity of aldehyde or ketone which is decomposed during the first hour. Results seem to show that steric influences do not affect this reaction, and that the degree of unsaturation of the carbonyl group depends upon differences in the relative strength of the partial valencies rather than upon differences in the electrochemical character of the atoms.

It was observed that the carbonyl group is most inert when present in acid derivatives, especially esters and chlorides. In general, compounds which contain carbonyl in close proximity to CH_3, CH_2R, or CHR_2 were found to be very unreactive. The highest degree of unsaturation was observed in the case of substances which contain carbonyl in union with unsaturated groups as, for example,

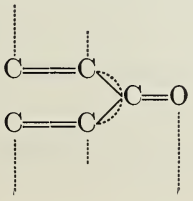
$$C_6H_5CH{=}CHCOC_6H_5 \quad \text{and} \quad (C_6H_5CH{=}CH)_2CO, \quad \text{etc.}$$

although aromatic ketones, such as benzophenone $(C_6H_5)_2CO$, and aldehydes of the type RCHO, are also reactive.

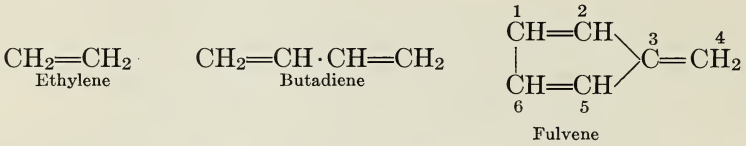
In the case of unsaturated ketones the reactivity is not limited to the carbonyl group, but extends to the entire conjugated system. To illustrate, $C_6H_5CH{=}CH_2$ and $C_6H_5CH{=}O$ react only slightly with diphenylketene, while $C_6H_5CH{=}CHCOC_6H_5$ reacts with extraordinary ease, a difference which may be readily understood by reference to the partial valency formulas of these substances, viz.,



Systems of crossed double bonds were observed to be even more reactive than simple conjugate systems. Dibenzalacetone represents such a system, the general partial valency formula of which is

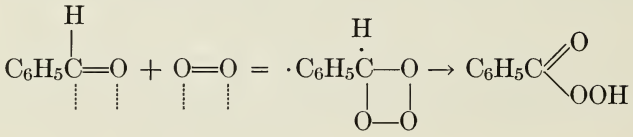


To recapitulate, substances possessing conjugate systems of double bonds are more reactive than substances with simple bonds, while most reactive of all are substances containing systems of crossed double bonds. This statement is further illustrated by the fact that butadiene is more reactive than ethylene, while fulvene is the most reactive of these three combinations:



The same relative difference in the degree of unsaturation has been noted in the case of simple ketones, diketones, and triketones where the carbonyl groups occupy adjacent positions. The fact that an increase in the unsaturated character of substances is frequently associated with the appearance of color will be considered later in the chapter on " Color and Constitution."

Staudinger,[1] by careful investigation of the reactivity of carbonyl in aldehyde combinations, found that diphenylketene and oxalyl-chloride interact more easily with *p*-methoxy- and *p*-dimethylamino-benzaldehyde than with benzaldehyde. In other words, substitution in the benzene nucleus increases the unsaturation of carbonyl, and consequently strengthens the partial valencies of this group, a principle which was confirmed by Staudinger in his work on autoxidation of aldehydes. According to C. Engler[2] the autoxidation of an aldehyde may be expressed as follows:



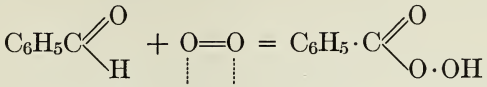
Since methoxy- and dimethylaminobenzaldehyde are more reactive towards ketene than benzaldehyde, exhibiting greater partial valency, it might be predicted that these two aldehydes would be more susceptible to oxidation than benzaldehyde. Staudinger found, however, that the reverse was true and that the aminoaldehyde was less reactive than anisaldehyde and the latter more stable than benzaldehyde. To explain these results he adopted an assumption made by Baeyer

[1] Ber., **46,** 3520 (1913).

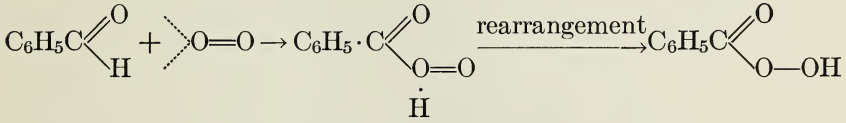
[2] " Kritische Studien über die Vorgänge der Autoxydation," pp. 89, Braunschweig, 1904.

and Villiger, that oxygen adds to aldehydes unsymmetrically, and interpreted the mechanism of this reaction (autoxidation) as follows:

Equation of Baeyer and Villiger:

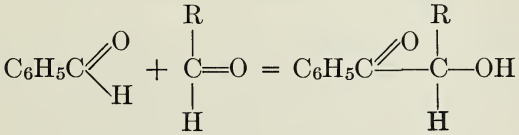


Staudinger's equations:



According to Staudinger, this explanation is strictly in accord with Thiele's theory of partial valency. In the two aldehydes, C_6H_5CHO and $(CH_3)_2N \cdot C_6H_4CHO$, the hydrogen of the latter is much more firmly bound than in benzaldehyde and shows less tendency to add to oxygen; consequently this aldehyde is less susceptible to oxidation influences than benzaldehyde. In other words, unsaturation of carbonyl groups connotes a firm union between carbon and hydrogen of the —CHO radical. Of the three isomeric aldehydes, $CH_3O \cdot C_6H_4 \cdot CHO$, the *o*-derivative was found to be the most resistant, and the *m*-compound intermediate between *o* and *p* in their reactivity towards oxygen. In other words, the *o*-compound contains the most unsaturated carbonyl group.

Staudinger [1] expresses the formation of benzoin from benzaldehyde according to the principle of autoxidation as follows:

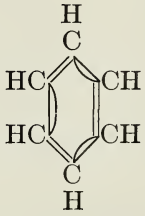


According to this interpretation, only aldehydes, which contain relatively unsaturated carbonyl groups and also relatively mobile hydrogens, polymerize with formation of benzoins. Benzaldehyde, anisaldehyde and *p*-chlorbenzaldehyde behave in accord with this principle. Dimethylaminobenzaldehyde, on the other hand, does not polymerize to a benzoin, although it contains a strongly unsaturated carbonyl group. If, however, this is mixed with another aldehyde, which contains a sufficiently mobile hydrogen atom, as benzaldehyde, anisaldehyde or *p*-chlorbenzaldehyde, mixed benzoin combina-

[1] Ber., **46**, 3535 (1913).

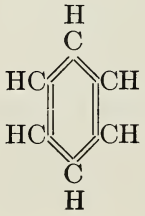
tions are formed. These somewhat meager illustrations help to show how fruitful Thiele's theory has been in the elucidation of problems in the chemistry of aliphatic combinations. It also serves an even more important function in connection with the chemistry of benzene and its derivatives.

The more important aspects of Baeyer's theory in regard to benzene have already been referred to. Kekulé's formula for benzene, with its three pairs of double linkages, failed to account for the saturated character of the substance, and this failure was the more striking because hydro-derivatives, possessing one and two pairs of double bonds respectively, showed typically unsaturated properties. In order to explain this difference in behavior Baeyer, in conjunction with Armstrong, advocated the so-called " centric formula " for benzene, in which six valencies were represented as mutually saturating each other, but he was unable to offer a rational explanation as to how the saturation of the six valencies was effected. Such an explanation is, however, possible in terms of Thiele's theory, according to which Kekulé's formula for benzene becomes:



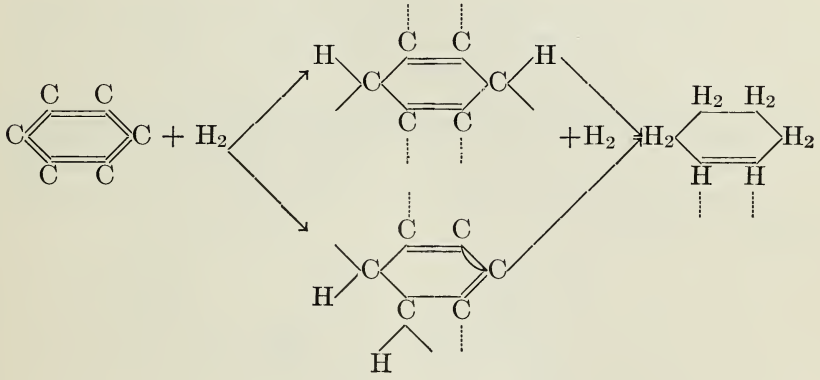
the six partial valencies being represented as united to form three " inactive double bonds."

That a substance possessing such a system of conjugate double bonds should be saturated in character is obvious. In the words of Thiele: " the saturation of the partial valencies renders the original three pairs of unsaturated double bonds inactive, so that it becomes impossible to distinguish any difference between them and the three secondary double linkages." Benzene may then be represented by the formula:



Such an expression obviates all need for "Kekulé's oscillation hypothesis" since it does not presuppose a difference between the *ortho*-positions 1–2 and 1–6.

Thiele's theory of partial valencies not only explains the saturated character of benzene, and the identity of the two *ortho*-positions in its molecule, but also allows for a satisfactory interpretation of reduction phenomena. The transformation of the saturated benzene nucleus into its unsaturated hydro-derivatives may be readily understood by referring to the partial valency formulas of the latter, viz.:



These formulas elucidate the thermal relationships already alluded to in this text and also explain the observed similarity between the *ortho*- and *para*-positions as well as the isolation of the *meta*-position.[1]

As has been stated 1–4 addition takes place in the system C=C—C=C because free residual affinity exists at these points.
1 2 3 4
Addition to the benzene ring, on the other hand, involves a disruption of the entire system and may result in either 1–2 or 1–4, but never 1–3 addition. The conditions which determine the direction which addition reactions will take in any particular case have not as yet been determined with accuracy. The simultaneous appearance of *ortho*- and *para*-substitution products can easily be understood in the light of this theory if, as Armstrong[2] assumes, the process of substitution consists primarily in addition reactions which are accompanied by intermolecular rearrangements and which ultimately result in the

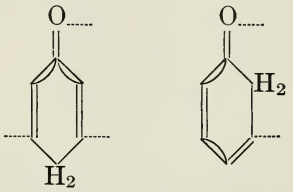
[1] Ber., **17**, 2719 (1884); Armstrong, Jour. Chem. Soc., **51**, 258,583 (1887); Morley, Ibid., **51**, 579; Crum, Brown and Gibson, Ibid., **61**, 367 (1892); Flürscheim, Jour. prakt. Chemie, **66**, 321 (1902); also see **71** and **76**.

[2] Jour.. Chem. Soc., **51**, 258 (1887).

splitting off of simple molecules. The application of Thiele's theory to a few individual aromatic compounds may now be considered.

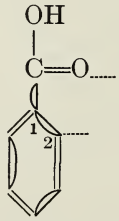
In spite of the fact that phenol contains a saturated benzene ring, as its formula shows,

it is an exceptionally reactive substance. This property vanishes, however, if the hydrogen of the hydroxyl group is replaced by substituents such as CH_3, C_2H_5, CH_3CO, etc. Now the group —C=C·OH which is present in phenol, readily rearranges, in the case of compounds of the aliphatic series, to give the system —CH—C=O. A similar rearrangement in the case of phenol would result in the formation of a substance possessing either one or the other of the following formulas:



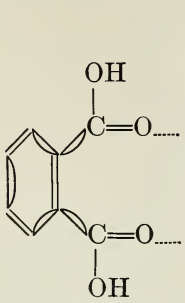
Both formulas indicate the presence of free residual valencies in the molecule, and it is perfectly reasonable to suppose that the chemical activity of free phenol depends upon a condition of tautomerism involving dynamic equilibrium between the *enol* and the more active *keto* forms.

Aromatic acids contain carboxyl groups in direct union with doubly-linked carbon atoms, and this condition gives rise to a system of crossed double bonds,



with a partial valence on the oxygen atom of the carbonyl and another, somewhat smaller partial valence on carbon in the nucleus. Addi-

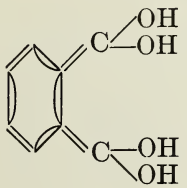
tion to such a system may be illustrated by the action of hydrogen on *ortho*- and *para*-phthalic acids:



Phthalic acid

Paraphthalic acid

In both instances the hydrogen may be supposed to add to the partial valencies on the oxygen, giving,



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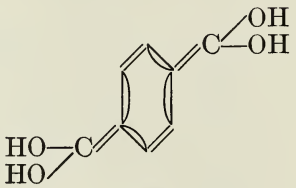
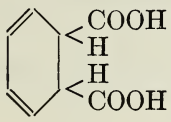
and



II

but this is followed immediately by rearrangements which result in the formation of the final products, viz.:



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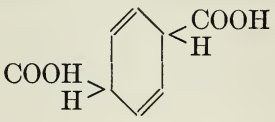
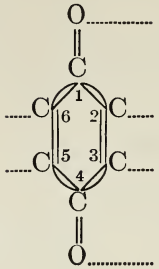


II

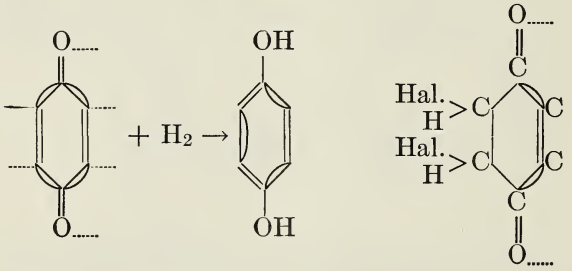
In the case of the corresponding aldehydes the course of the reaction is the same, but reduction takes place much more readily.

Experience has shown that certain hydrogen atoms of the benzene ring are very mobile in quinone,[1] but this fact finds no satisfactory explanation in the formula commonly assigned to this substance. Reference to the partial valency formula, however, shows at once that four small residual affinities are present on the carbon atoms 2, 3, 5 and 6, and two others, relatively greater, on the oxygen of the carbonyl group:

[1] Ber., **31**, 978 (1898).

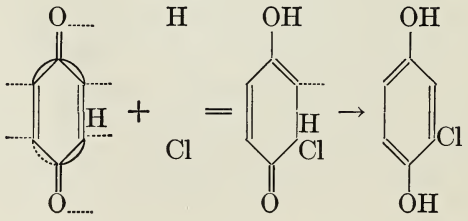


It is obvious that additions in the 1–4 positions are impossible. The course taken in addition reactions depends in great measure upon the chemical nature of the adding atoms or groups of atoms. Thus, for example, hydrogen adds primarily to oxygen, as is shown by the formation of hydroquinone, while halogen, on the other hand, shows an affinity for carbon and adds in the **5–6 position**, forming dihalides corresponding to the formulas below:



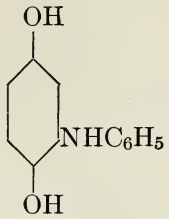
Since the formation of such substances is accompanied by a decrease in the free energy in the molecule, due to loss of residual valencies in positions 2 and 3, the addition of a second molecule of halogen should take place less readily than in the case of the first, and this is, in fact, true.[1]

In the addition of hydrogen chloride to quinone, hydrogen adds to oxygen and chlorine to carbon. Thus



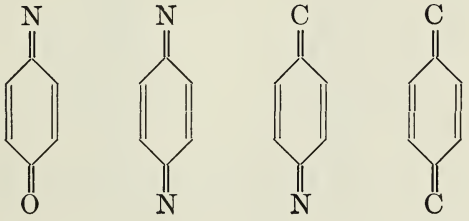
[1] Nef. Jour. prakt. Chemie, **42**, 182.

aniline adds in a similar manner to form

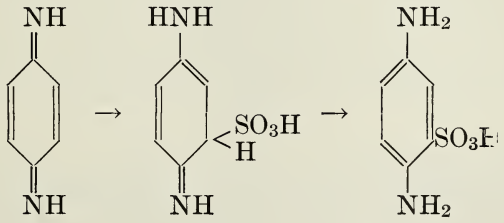


as a primary product.

If the oxygen of quinone is replaced wholly or in part by nitrogen or by carbon, the following types result:

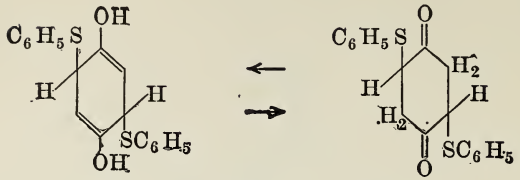


Such atomic systems are present in a great variety of colored compounds, and show properties analogous to those observed in the case of quinone. Thus, for example, sulphurous acid reacts with quinonediimide to form a sulphonic acid derivative of *p*-phenylene diamine.



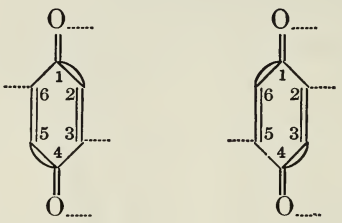
Th. Posner[1] uses formulas which differ slightly from those of Thiele. For example, when thiophenol reacts with quinone, an addition product consisting of two molecules of thiophenol and one molecule of quinone is formed, to which Posner assigns the following tautomeric formulas:

[1] Annalen der Chemie, **336**, 106 (1904); Jour. prakt. Chemie, **83**, 471 (1911).



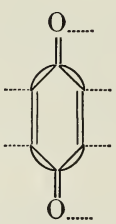
Enol form Keto form

Posner's theory in regard to the distribution of affinity allows for tautomerism of still another type. He supposes that quinone, and all true derivatives of quinone, are able to exist in two tautomeric forms:



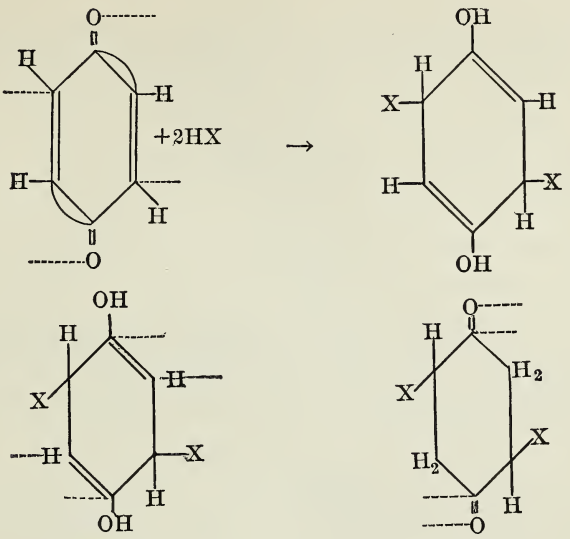
I II

A comparison of these formulas with that of Thiele



shows a slight difference in one respect. Thiele assumes that the free residual affinity on the carbon atoms 1 and 4 is distributed equally on two sides, thus saturating the atoms 2–6 and 3–5 respectively, while Posner imagines that this affinity acts as a single force to saturate in the one case 2 and 5 (I) and in the other, 6 and 3 (II).

The addition of halogen hydrides, aniline and other substances to quinone and derivatives of quinone is supposed by Posner to take place in a manner strictly analogous to that which has just been described in the case of thiophenol.



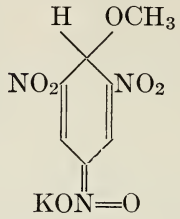
All these addition products behave in a tautomeric manner and are able to pass readily into true derivatives of benzene. Addition, according to Posner, represents the first phase of the change. The transformation into true benzene compounds is the second phase and involves a loss of hydrogen, giving dihalogenated hydroquinones, dianilinonoquinone, etc.

Tautomerism of the *enol-keto* type may be supposed to account for the existence of colorless and colored compounds as well as for variations in the intensity of color in the case of substances possessing quinoidal structure. Since the *keto* is the more unsaturated of the two tautomeric modifications, this arrangement may be assumed to be the one which is present in a strongly colored substance belonging to this class.

An elucidation of the chemistry of aromatic nitro-compounds was effected by Meisenheimer [1] by the use of partial valency formulas. Up to this time no rational explanation had been offered for the fact that trinitrobenzene and similar substances dissolve in alcohol in the presence of a base, to give salts, which, when isolated, are always found to contain residues of the given alcohol. Meisenheimer interprets this phenomenon by supposing that the reaction is one of simple addition. He assumes that the reactivity of the carbon atom in the *para*-position with respect to NO_2 is greatly augmented by the introduction of

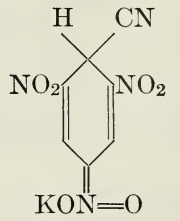
[1] Annalen der Chemie, **323**, 219 and 241 (1902).

other nitro-groups, and that K and OCH_3, for example, add respectively to the free affinity which is present on carbon and oxygen, forming

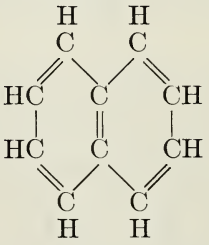


An analogous configuration may be assigned to the salt formed by the action of potassium methoxide upon trinitroanisol, etc. The cases of nitro-naphthalene and anthracene will be reserved for somewhat more detailed discussion later.

Potassium cyanide also reacts with the more highly nitrated derivatives of benzene and naphthalene in a manner analogous to that which has just been considered in the case of potassium methoxide. Red salts are formed to which, in the case of trinitrobenzene for example, the following formula has been assigned:



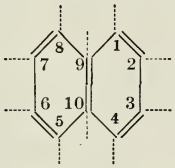
The most generally accepted formula for naphthalene is that which has been proposed by E. Erlenmeyer, Sr., and which assumes the presence of two condensed benzene nuclei:



According to this formula naphthalene might be expected to resemble benzene very closely in its chemical properties. Bamberger has shown, however, that naphthalene is much more reactive than benzene, and that in the presence of reducing agents, for example, it readily adds first

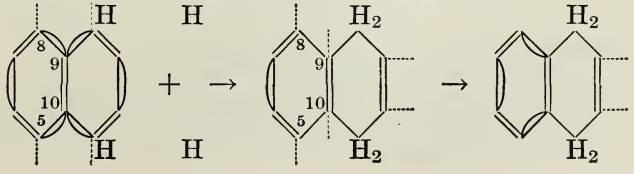
two and then four hydrogen atoms. Further additions of hydrogen do not take place so readily, and this is explained by supposing that tetrahydronaphthalene contains a true benzene nucleus, thus offering increased resistance to the action of reducing agents. The rather remarkable course of this reduction was originally interpreted by Bamberger in terms of his theory of potential valencies, but this theory proved inadequate to explain the further observation of Bamberger that additions of hydrogen and other atoms always take place in the α-positions. A more satisfactory and rational interpretation of the phenomenon is offered by Thiele's theory of partial valencies. This may be developed in brief as follows:

According to the Erlenmeyer formula for naphthalene, partial valencies are assumed to exist on all of the ten carbon atoms,



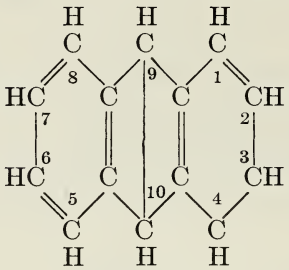
If. however, such free valencies are imagined as uniting to form conjugate systems it becomes apparent that the free affinity on the carbon atoms 2, 3 and 6, 7 is fully equalized. The partial valencies of 9 and 10 do not, however, suffice to fully saturate those on both 1 and 8 and 4 and 5 respectively. Thus, while the total affinity on 9 and 10 is completely neutralized, carbon atoms 1 and 4 and also 5 and 8 possess residues of affinity. In other words, partial valencies may be imagined as present on all α-carbon atoms as is indicated below:

These " half " partial valencies offer initial points of attack to adding atoms or groups and the phenomenon of 1–4 addition is therefore readily explained. In reduction, for example, the course of the reaction may be represented by means of the following scheme:



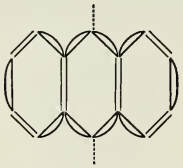
This formulation shows not only why primary addition takes place in the α-positions, but also why four and only four atoms add with relative ease. The formation of a true benzene nucleus in dihydronaphthalene, as shown above, readily explains the resistance of tetrahydronaphthalene to the further action of reducing agents.[1]

According to the usual formula for anthracene,

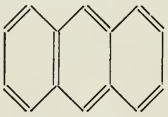


this substance might be expected to be very unreactive, since, in addition to two benzene nuclei, the molecule contains only carbon atoms in simple forms of combination. As a matter of fact, however, the carbon atoms in the positions 9 and 10 are readily attacked by a variety of reagents, and in particular, by the lower oxides of nitrogen.[2]

Thiele's theory affords a rational explanation of the chemical activity of the carbon atoms, by assuming the presence of free affinity at these points. His formula for anthracene does away with the necessity of a single bond between the carbon atoms 9 and 10 as shown above, and represents the molecule as composed of carbon atoms united by means of conjugate systems of double bonds:[3]



It is of interest to call attention here to an *o*-quinoidal formula for anthracene which has been proposed by Armstrong, and which



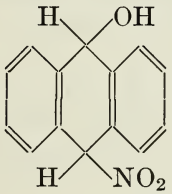
[1] Meisenheimer, Annalen der Chemie, **323**, 218 (1902).

[2] Annalen der Chemie, **323**, 205 (1902); **330**, 133 (1904).

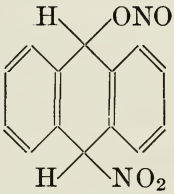
[3] Annalen der Chemie, **306**, 141 (1899); also compare K. H. Meyer's recent work in Annalen der Chemie, **379**, 37 (1910); **396**, 133, 152, 166 (1912); and Annalen der Chemie, **420**, 113, 126, 134 (1920).

has recently received support through the spectrochemical researches of Auwers.[1]

By means of the Thiele formula Meisenheimer has been able to elucidate the action of the lower oxides of nitrogen upon anthracene. In 1880 Liebermann and Lindemann[2] treated anthracene with the oxides of nitrogen in the hope of getting nitro-derivatives. Two different products were obtained, depending upon the conditions of the experiment, namely, what may be called an anthracene nitrate of formula $C_{14}H_{10}\cdot HNO_3$, and anthracene nitrous oxide, $C_{14}H_{10}N_2O_4$. Meisenheimer has since shown that both of these compounds are true derivatives of anthracene and correspond structurally to the formulas[3] I and II respectively:

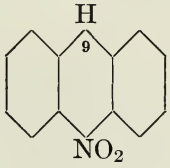


I



II

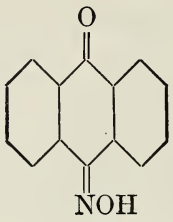
Both substances, when treated with sodium hydroxide, give the same product, which Liebermann and Lindemann called nitrosoanthron, but which the later researches of Meisenheimer and Dimroth[4] have shown to be nitroanthracene:



This substance has also been obtained by Perkin,[5] who prepared it by nitrating anthracene in alcohol and decomposing the resulting product with alkali. Both Liebermann and Perkin observed that in addition to nitroanthracene, which is insoluble in alcohol, a soluble product was formed during the course of these reactions. This was called nitrosohydranthron and given the empirical formula, $C_{14}H_{11}NO_2$ by the first investigator, while the latter called it pseudonitrosoanthron and gave it the formula $C_{14}H_9NO_2$.

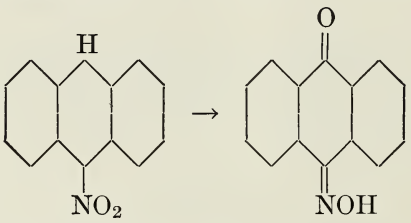
[1] Ber., **53**, 941 (1920).
[2] Ber., **13**, 1584 (1880).
[3] Ber., **33**, 3547 (1900).
[4] Ber., **34**, 219 (1901).
[5] Jour. Chem. Soc., **59**, 634 (1891).

Meisenheimer[1] has since shown that nitrosohydranthron and psuedonitrosoanthron are identical, that they correspond to Perkin's formula and that they may be regarded as a monoxime of anthraquinone:

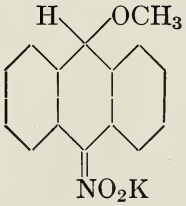


He was able to show further that the substance could be prepared in any desired quantity by treating nitroanthracene with potassium methylate in methyl alcohol solution.

The transformation of nitroanthracene into the monoxime of anthraquinone may be regarded as a change which involves intramolecular oxidation and which results in the formation of a nitrosophenol, which then rearranges to the oxime.

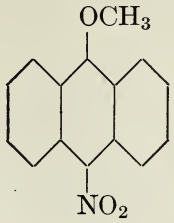


It is very improbable, however, that this represents the true mechanism of the reaction, since when nitroanthracene is treated with potassium alcoholate, secondary products containing methoxy-groups are formed. By changing the conditions of the experiment it is even possible to obtain such substances as the principal products of the reactions. Thus, for example, if nitroanthracene is shaken with a solution of potassium in methyl alcohol it is transformed into a potassium salt having the constitution represented by the formula:

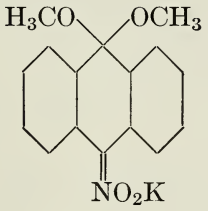


[1] Annalen der Chemie, **323**, 204 (1902).

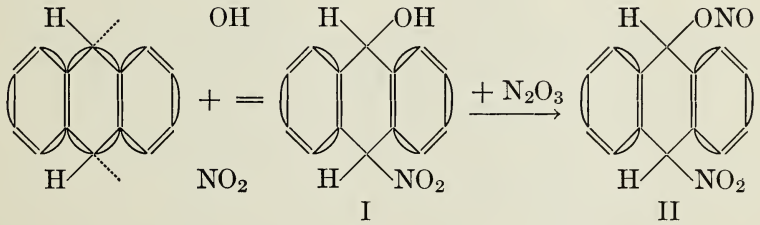
This salt is, in fact, an addition product, and may be regarded as the metallic derivative of nitromethoxyanthracene,



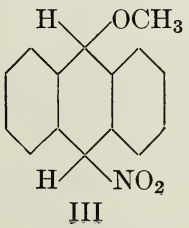
It can indeed be obtained from it. Prolonged treatment of nitroanthracene with potassium methoxide leads to the addition of a second molecule of potassium methoxide and results in the formation of a substance having the formula:



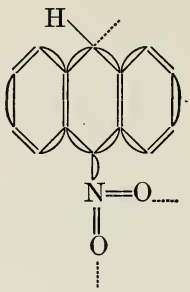
These reactions may be readily explained on the basis of Thiele's theory of partial valencies. The reaction between anthracene and nitric acid is imagined as taking place according to the following scheme:



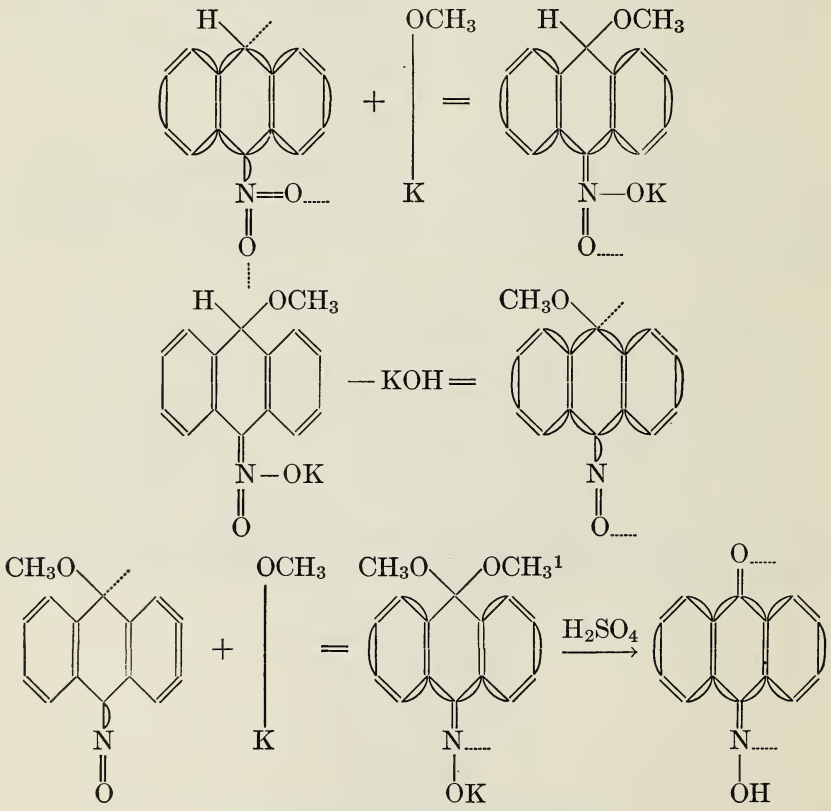
Either substance (I or II) when treated with methyl alcohol will give dihydronitroanthranol methyl ether,



by the substitution of a methoxy-group for an OH or an —ONO group respectively. By loss of H_2O, HNO_2, or CH_3OH respectively, each of these three substances may in turn be transformed into nitroanthracene:

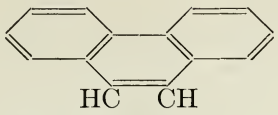


The formation of the oxime of anthraquinone and of nitroanthrondimethylacetal from nitroanthracene may be considered as taking place according to the following scheme:



[1] For further details consult Annalen der Chemie, **355**, 249 (1907).

The commonly accepted formula for phenanthrene,



supposes that three complete benzene nuclei are present in a molecule of the hydrocarbon. This structure does not account, however, for the marked reactivity of the two central carbon atoms. Thiele's formula for phenanthrene, on the other hand, shows that the affinity of these two carbon atoms is only partially saturated, and that each therefore possesses a residue of free chemical affinity. On this basis their reactivity is readily understood.[1]

Other ring systems may obviously be explained in the terms of Thiele's hypothesis but the present discussion must be limited to those which have just been considered. The relations existing between the physical constants of the chemical compounds represented by the various systems of combination of atoms will be considered in some detail in later chapters.

From the very beginning Thiele's theory has been the subject of violent controversy and, as a result, has been modified in several important respects. The basic principle of the hypothesis still holds and its application has served to account for many phenomena which would have been inexplicable without it. It has been of still greater service in opening new channels for the further development of the theory of organic chemistry.

Following the appearance of Thiele's theory, E. Knoevenagel[2] and E. Erlenmeyer, Jr.,[3] attempted to explain all of the phenomena with which it dealt by means of stereochemical conceptions. These ideas were considered in some detail in an earlier edition of the present text but will be omitted from this text because no use has been made of them in the intervening time and they have undergone no further development. All stereochemical assumptions demand so many special hypotheses which cannot be proved that it is questionable whether they help to elucidate a given problem or confuse it.

When compared with other theories which have been advanced to explain the phenomena of unsaturation, Thiele's assumption of partial valencies—or, in other words, fixed positions of free affinity on the atom—may be said to represent the simplest working hypoth-

[1] See: Ber., **33** and following for the work of J. Schmidt and A. Werner.

[2] Annalen der Chemie, **311**, 203 (1900); Ber., **36**, 2806 (1903).

[3] Annalen der Chemie, **316**, 50.

esis known at the present time if we accept the idea of residual affinity or partial valency. It is especially valuable when used in conjunction with certain definite conceptions in regard to the specific relationships which exist between the different atoms, but this is a matter which will be referred to again later. It may be said at this point, however, that the form in which Thiele's theory is most frequently used at the present time is one which represents an extension of Thiele's original conception by the injection of certain other fundamental ideas. The latter embody what is known as Werner's theory and must now be considered in some detail.

CHAPTER V

THE THEORY OF ALFRED WERNER

Researches in Organic Chemistry led, in the second half of the last century, to the supposition that the valency of carbon was always four, and could be represented by four separate forces acting in definite directions in space. This hypothesis is open to many objections and in 1881, it was vehemently attacked by A. Claus.[1] To quote his words, "facts support the assumption that the carbon atom functions ordinarily as a tetravalent element, but to suppose that the chemical attraction inherent in its atom is divided into parts each of which acts independently of every other is as unnatural as it is unfounded." It seemed much more rational to Claus to suppose that the total affinity of carbon is unified and acts as one force, separating into parts only when carbon enters into combination with other atoms, in which case the partition that takes place is determined to a large extent by the relative affinity of the reacting atoms. Thus, for example, in such compounds as CO_2, CS_2, etc., the chemical energy of carbon may be regarded as divided into two equal parts, because the two atoms with which it is combined are alike; while in the compound COS the two affinities of carbon, which are exercised in holding oxygen and sulphur respectively, are unequal because the chemical energies of these two elements are different.

The objections raised by Claus and by others[2] were unheeded at the time because the attention of chemists was centered in the controversy as to whether the carbon atom was to be regarded as a sphere with valencies directed toward the corners of a tetrahedron, or as itself a tetrahedron with valencies situated in the corners or on the sides.[3] And since this controversy was productive of valuable experimental results, ten years elapsed before there was any further theoretical amplification of this fundamental idea of Claus. In 1891 A. Werner finally succeeded in formulating a theory[4] which has

[1] Ber., **14**, 432 (1881).

[2] Lossen, Annalen der Chemie, **204**, 327 (1886); Ber., **20**, 3306 (1887).

[3] Wunderlich, "Konfiguration organischer Moleküle," Wurzburg, 1886.

[4] Vierteljahrsschr. d. naturf. Ges. in Zürich, **36**, 129 (1891); "Neuere Anschau-

received very wide and increasing recognition and by means of which it has been possible to interpret the chemical properties of compounds containing asymmetrical cobalt, rubidium and other atoms. Although this theory has developed in connection with phenomena in the field of Inorganic Chemistry, it is also applicable to Organic Chemistry and is beginning to be used more and more in the interpretation of organic problems.

According to Werner, an atom may be regarded as spherical, homogeneous and of definite size. The idea of four individual valencies operating in definite directions in space is replaced by the view that the property of attraction emanates from the center of the atom and is evenly distributed over its surface. A *priori*, there is no division of this attractive force into separate parts. In the case of the carbon atom, Werner believes that evidence goes to show that it can attract and hold, at most, four other atoms. If four atoms combine with a carbon atom they will distribute themselves so as to produce the greatest possible neutralization of their reciprocal affinities, and the surface attraction of the carbon will divide itself among the various atoms according to their nature. Each fractional part of the total affinity of the carbon atom, may, therefore, be regarded as distributed over a definite sector of the surface of the sphere representing the mass of the atom, and constitutes the so-called "Bindefläche" (combining surface) of the atom. The intensity of this surface attraction varies in the different elements. The most stable arrangement of atoms will be that in which the largest part of the surface of the central sphere is covered, without an overlapping of the segments, and, on the other hand, chemical union between two atoms will be weakened if the combining surfaces of the atoms are only partially covered by their reciprocal attractions.

If all four atoms attached to carbon are similar, as in methane, each will require an equal amount of surface attraction, and they will, therefore, arrange themselves around the central carbon atom in the form of a regular tetrahedron. This represents the most stable arrangement for carbon, since any displacement of an atom from its position at the corner of the tetrahedron brings about a condition where the lines of force emanating from the central atom are only partially neutralized by the reciprocal attraction emanating from the combining atom, and thus the union between the two atoms is weakened.

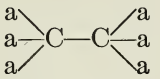
If any of the four atoms in union with carbon are different, as in

ungen auf dem Gebiete der anorganischen Chemie," Braunschweig, Fr. Vieweg & Sohn, 3d Ed. 1913.

$CR^{I}_{2}\ R^{II}_{2}$ and $CR^{I}\ R^{II}\ R^{III}_{2}$, the distribution of affinity will be irregular; and if all four atoms are different as in $CR^{I}\ R^{II}\ R^{III}\ R^{IV}$ an asymmetric tetrahedral grouping of the atoms will result, and two enantiomorphic configurations will be possible. The theory is thus able to account for the existence of space isomers. The new conceptions developed by Werner to explain the mutual rearrangement of optical or geometrical isomerides can not, however, be discussed at this time.

The nature of the union between the carbon atoms in compounds containing single, double and triple bonds must now be considered in detail in the light of Werner's theory, and an effort must be made to see whether the theory is able adequately to explain the facts observed in regard to the relative strength of the various types of union.

In the case of so-called single union between two carbon atoms—as, for example, in the system:



—the full force of affinity will be exerted only at the points of contact of the two carbon atoms, and at every other point on the hemispheres the strength of affinity will be represented by the component of the total affinity which is parallel to the axis joining the centers of the two spheres. In Fig. 1 the force of affinity at the point where the dotted line meets the circumference of the sphere may be resolved into two forces, C_1 and C_2, of which C_1 alone will be active in binding the two carbon atoms.

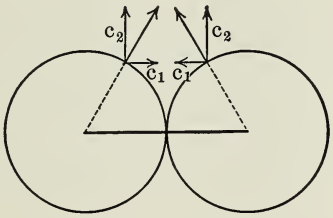


FIG. 1.

The value of this force gradually decreases as the distance between the surfaces of the atoms increases, thus leaving an amount of free affinity which E. Bloch [1] has estimated "at less than one-half and more than one-third of the bound energy which is exercised in actually holding the atoms together"[2] (i.e., represented in the mutual saturation of their valencies).

[1] "A. Werner's Theorie der Kohlenstoffatoms," p. 14, Leipzig, 1903.

[2] A. Werner, Ber., **39**, 1278 (1906).

In the case of so-called double bonds, as for example, in the system $(a)_2C{=}C(a)_2$, it is assumed that the two carbon atoms are bound together by that part of the total affinity of each carbon atom which is left after deducting from the total the amount of affinity necessary to hold the substituents. This residue is greater than the amount of free affinity neutralized in the simple union between two carbon atoms. Werner[1] subdivides it into two parts, of which one is situated outside the combining zones of a and a (represented by x, and x', in Fig. 2), and the second, in the segment between a and a (represented by α and α', in Fig. 2).

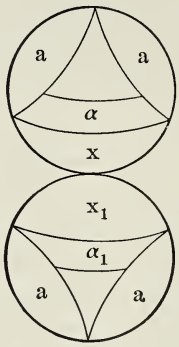


Fig. 2.

The forces radiating from x and x', act so uniformly that the two atoms are able to revolve about a common axis. The forces radiating from α and α', however, are not so symmetrically distributed and under certain conditions must interfere with the free rotation of the atoms. The latter fact is without stereochemical significance. According to Bloch, in the case of a double bond the amount of free affinity is nearly equivalent to that which is bound and is relatively three or four times as great as the free affinity estimated in the case of single bonds.

By a similar disposition of two spheres, Werner represents trebly bound carbon as in the acetylene series, $aC{\equiv}Ca$, but since only one other atom is attached to each carbon sphere the amount of affinity left for binding the two atoms together is greater than in the case of the singly or doubly-linked carbon systems. Bloch found that the amount of free affinity is twice as great as that which is bound, and is relatively twice as great as the free affinity estimated for the double bond and six times that estimated for the single linkage. According

[1] Vierteljahrsschr. d. naturf. Ges. in Zürich, **36**, 145.

to this conception, the amount of affinity neutralized in the manifestation of double and triple bonds is greater than in the case of single bonds, and this appears to be in harmony with the fact that acetylene is stable at high temperatures. To account for the relatively greater reactivity of the so-called unsaturated compounds, Werner makes a distinction between stability and reactivity. Thus reactivity is determined by the amount of free affinity present on the atom (see component C_2, Fig. 1), and is greater for derivatives of ethylene and acetylene than for derivatives of ethane.[1] It may be imagined as radiating beyond the contour of the molecule, and in this way operating to attract other atoms to the molecule and so to bring about chemical action. From these considerations it is obvious that the triple bond produces the most reactive, the single bond, the least reactive molecule. Werner points out, however, that the amount of free affinity is not a constant either for singly or doubly bound carbon but that it varies according to the nature and constitution of the particular compound.

Three or more carbon atoms may enter into combination to form either a chain or a ring. This may be formulated in the terms of Werner's theory as follows: " If the atoms uniting with carbon attract each other only slightly or not at all, the valencies may be regarded as operating through the corners of a regular tetrahedron. If, however, the valencies are deflected from these positions, the stability of the union with carbon is lessened, and this is the case in many ring compounds. The tension in ring compounds observed by von Baeyer may be explained in terms of Werner's theory as due to the tendency on the part of the atoms to return to positions of the greatest possible neutralization of their affinities, and von Baeyer's law governing tension in such cases harmonizes with Werner's conceptions in all essentials.

The increased reactivity of hydrogen atoms in union with doubly and trebly bound carbon may be regarded as analogous to the mobility of the α hydrogen present in acids of the general formula $\rangle CH \cdot COOH$. The latter has been interpreted by Werner[2] as due to the fact that the oxygen atom in the carbonyl group requires a relatively large part of the combining surface of the carbon atom so that only a relatively small part of the affinity of the carbon is available for holding the adjoining carbon atom. The result is to increase the total amount of free affinity on this second carbon atom. Since free affinity is to be regarded as radiating beyond the contour of the molecule, it is obvious that the substance will exercise an increased attraction for other atoms.

[1] Ber., **39**, 1278 (1906).

[2] Theorie der Kohlenstoffatoms, p. 166

The groupings C=N and C=C exert an influence analogous to that of C=O. Bloch [1] believes that stereochemical explanations should not be sought in such cases, and interprets the reactivity of the α hydrogen as due to the acidifying influence of the double bonds.

In the case of conjugated double bonds, as, for example, in the system C=C—C=C, there would be less free affinity on the two middle than on the end carbon atoms, so that the phenomena may be interpreted in much the same way in terms of Werner's theory as in terms of the theory of partial valencies as developed by Thiele.[2]

Werner conceives that in benzene the six carbon atoms are joined together in the form of a ring, the constitution of which may be represented by Fig. 3.

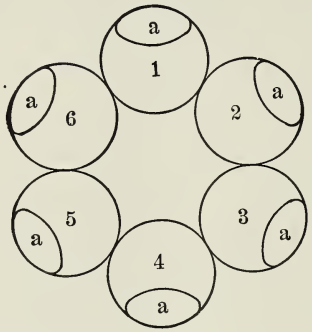


Fig. 3.

Because the six carbon atoms are combined in the same ring, each comes within the sphere of attraction of every other, and, at the same time, any movement outside of this sphere of attraction is restricted. And since in benzene every carbon atom is exactly equivalent to every other in its combining power, the static condition of the molecule will be that in which each and every atom is bound to its respective position by the exercise of the greatest possible fraction of its total affinity, although the value for this fraction may vary for the individual atoms.

Werner pictures the reciprocal exchange of chemical affinity between the carbon atoms of the benzene ring in the following way: "The force of attraction emanating from a carbon atom is comparable to the emission of light. Thus atom 1 may be imagined as luminous and as radiating light upon the other five. It follows that of these, the carbon atoms in the *ortho*-positions (atoms 2 and 6) will receive the same, and, relatively to other atoms, the greatest illumination. The carbon

[1] Theorie der Kohlenstoffatoms, pp. 25, 26. [2] Ibid., p. 20.

atoms in the *meta*-position (atoms 3 and 5) are, on the other hand, partly shaded by the *ortho*-carbon atoms, and so receive very slight illumination. Moreover, the light which is received by these atoms is less intense because of the greater distance through which it must pass. Finally, the carbon atom in the *para*-position (number 4) receives a relatively great amount of direct light, but this light loses somewhat in intensity by reason of the distance through which it must travel."

This conception finds expression in the following hexagonal formula for benzene:

To quote Werner's words, " the six carbon atoms of the benzene ring may be assumed to lie in the same plane. The hydrogen atoms are also distributed symmetrically in this plane but are so arranged as to lie outside the ring. Carbon atoms in the *ortho*-positions are mutually saturated by the exercise of a somewhat greater fraction of their total affinity than is supposed to be represented in the ethylene type of combination. A small fraction of affinity, equal roughly to a partial valency, may be assumed to act between carbon atoms in the *para*-positions, and it may even happen that still smaller fractions enter into the mutual saturations of carbon atoms in the *meta*-positions."[1] It is obvious that these valencies correspond to neither single, double, nor diagonal bonds.

Such a formula may be said to resemble the Armstrong-Baeyer *centric* formula more nearly than any other which has been advanced to explain the chemical and physical properties of benzene, but it differs from it in certain respects. It seems indeed to embody an entirely new conception of the atomic relationships in benzene and its derivatives. Werner's conceptions have been somewhat amplified by E. Bloch and have been presented in such a form as to give a very comprehensive interpretation of the chemistry of aromatic compounds. As applied in the most diverse fields of organic chemistry by A. Werner, P. Pfeiffer, and E. Bloch, these conceptions have served to represent the most complicated relationships in such a way as to free them from the limitations frequently imposed by the use of structural formulas.

Werner has been unusually successful in the application of his theory in the field of inorganic chemistry and has been able to break down

[1] " Handwörterbuch der Naturwissenschaften," 1915, p. 178.

the wall of separation between so-called molecular and atomic compounds. The mechanism by which whole molecules of apparently saturated compounds are held together is inexplicable in terms of the usual conceptions of structural chemistry but is, on the other hand, readily comprehensible in terms of Werner's theory, since this assumes that the atoms which are bound together in the various forms of saturated combinations still possess residual valencies and are therefore capable of further reactions.

As has been noted, Werner regards the valency of each atom as distributing itself in such a way as to satisfy not only the affinity of the contiguous atoms but also certain necessities in the special arrangements of these atoms in the molecule. First of all, he distinguishes between compounds of the first order and of the second order by supposing that, while the former represent compounds in which the principal valencies of the respective atoms are saturated, this does not necessarily exhaust the affinity at the disposal of the atoms in question. If further combinations take place, compounds of the second order will be formed. In developing this conception Werner has introduced the terms *principal* and *auxiliary* valencies to denote the above two kinds of combination. Principal valencies correspond to ordinary valencies and bind together such atoms or groups as are capable of existing as independent ions, or are equivalent to such ions, as for example

$$Cl, \quad Na, \quad NO_2, \quad CH_3, \text{ etc.}$$

Auxiliary valencies, on the other hand, represent an entirely new conception and may be expressed by means of dotted lines. They are met with in the case of such radicals as are capable of functioning as whole molecules and which cannot exist or function as independent ions, as for example

$$H_2O\cdots; \quad H_3N\cdots; \quad HCl\cdots; \quad O_2\cdots; \quad (CH_3)_3B\cdots;$$
$$(CN)_2Fe\cdots; \quad (CN)_3Fe\cdots; \quad \text{etc.}$$

These radicals may be regarded as entering into chemical combinations only through the exercise of auxiliary or residual affinities.

The two kinds of valencies may be distinguished by their energy content, the principal valencies representing, in general, greater affinity than the auxiliary. The difference is, however, one of degree and depends upon the relative amount of saturation of the other valencies. Both types must be regarded as components of the total affinity of the atom, and there is no really sharp line of demarcation between them. They merge, and, under certain conditions, pass one

into the other, for it is obvious that the degree of saturation of one kind of valence must tend either to strengthen or weaken the other.

The number of principal valencies which a given atom is capable of exercising is not a fixed quantity, but depends upon the nature of the atoms with which it is in combination. This follows from the fact that the relative strength of combination between atoms varies with the nature of the atoms, and any change in the amount of affinity exercised by the valencies must be accompanied by a change in their number, if the total affinity of the atom in question is to be saturated. Thus iron, for example, has a maximum of three principal valencies for chlorine, while this number may be increased for oxygen. The total affinity exercised by the iron in each case may be regarded as the resultant of the strengths of attraction of all the atoms entering into chemical combination with it. Allowing for variation in the number of valencies, there is, nevertheless, a maximum number of principal valencies for each element.

Although only a relatively small part of the total affinity of the atom is needed in the exercise of auxiliary valencies, there exists, nevertheless, a maximal number for each element. In order to answer the question as to what factors govern the limiting value of this number in any given case, it is necessary to consider the conditions under which the saturation of such valencies takes place. Structural formulas are based upon the assumption that the radicals which unite to form a given chemical compound are adjacent to each other and in direct union. It is not necessary to suppose that such groups are immovable, but it must be assumed that no atom or group occupies wholly or in part the space which belongs to some other atom as its particular sphere of rotation. Now, if the atoms in a molecule are joined to a central atom by means of principal and auxiliary valencies, it follows from what has just been said that only a limited number will find places in the space immediately surrounding this central atom. The space contiguous to a central atom is spoken of as the " first sphere," and the atoms occupying positions within the first sphere may be regarded as in direct union with the central atom. The " coordination number " of the atom is the term used by Werner to express the number of atoms which, in a given case, can hold positions within the first or undissociable zone of the central atom. Such atoms or groups may be regarded as bound to the central atom either by principal or auxiliary valencies; they may also be bound to other atoms which occupy positions in the second or dissociable zone with respect to the central atom.

While the values of the coordination number of the different elements

may vary and, in case of a given element, may even be different under different conditions, only the *maximal* value need be considered at present. By this is meant the maximum number of atoms which are capable of combination in the first sphere. It is relatively independent of the nature of these atoms and is governed largely by the amount of space constituting the first zone. Those compounds in which the maximal value has been reached are said to be coordinately saturated. The maximal value of the coordination number of a given atom may be obtained from a study of the constitution of all of its known compounds, and in the case of a very great number of elements is equal to six. In the case of carbon, however, it is equal to four; and it has been found that the elements which occupy positions next to carbon in the Periodic System, namely, boron and nitrogen, also have coordination numbers equal to four. The coordination number and the number representing the principal valencies are identical in the case of carbon, but in the case of a very great number of other elements this is not true. Usually the coordination number (equal to 6) and the maximum number of *auxiliary* valencies are identical. Finally it should be noted that in many of the compounds of a given element its maximum coordination number is not reached, such compounds being spoken of as coordinately unsaturated.

The existence of partial valencies has been demonstrated in the case of substances which contain singly bound atoms as well as in the case of those having unsaturated groupings. This fact was first recognized by R. Anschutz,[1] but its general application was established by Werner. Suppose, for example, that the atom Me is attached to several atoms, among which is the atom X, by means of single unit valencies. If the character of its union with the other atoms is such as to engage a very large fraction of its total affinity, it follows that it will have relatively less affinity available for saturating the valency offered by X. The valency of X will not, therefore, be fully neutralized by its union with Me and the fraction of affinity which remains free may, under certain conditions, function as a partial valency in the formation of molecular compounds such as MeX . . . A.

In order to test the experimental accuracy of this deduction from his theory, Werner [2] first investigated inorganic compounds of the general formula MeX_n, where n represents the maximal number of valencies of the atom Me, and where the compound may, therefore, be regarded as apparently fully saturated. He was able to show that the halides SCl_4, $SeCl_4$, PBr_5, PCl_5 and others react readily with chlorides,

[1] Zeitschr. Electrochemie, **32**, (1904); and Annalen der Chemie, **346**, 397 (1906).
[2] Ber., **39**, 1278 (1905).

such as $AuCl_3$, $FeCl_3$, $AlCl_3$, $SbCl_3$, $SnCl_4$, etc., to form addition products of the formula $SCl_4 \cdot AuCl_3$, $SCl_4 \cdot FeCl_3$, $(SCl_4)_2 \cdot SnCl_4$, etc. From this Werner concluded that one of the halogen atoms in each member of the first series of compounds, as for example $ClSCl_3$, actually possesses the power of exercising a partial valency.

Organic halides have in numerous instances been observed to behave in the same way. Triphenylmethyl chloride, for example, reacts with chlorides, such as $ZnCl_2$, $AlCl_3$, $SnCl_4$, etc., to form addition products of the type

$$(C_6H_5)_3CCl \ldots SnCl_4$$

In the case of this particular substance the chlorine atom is so active that it enters into combinations with water, alcohol and other reagents. Werner was able to demonstrate that this reactivity is not conditioned by the negative character of the three phenyl groups, since tribenzoylmethylbromide $(C_6H_5CO)_3CBr$, contains an inactive halogen atom, but that it depends upon a weakening of the fourth valency of the methane carbon atom in the triphenylmethyl radical. Such a weakening of valency may be accounted for by supposing that almost all of the affinity of the methane carbon atom is required for the saturation of the three phenyl groups and that, therefore, very little is available for holding a fourth atom or group. This interpretation is further supported by the fact that the aliphatic hydrogen in triphenylmethane is much more reactive than a hydrogen in methane and the molecule is capable of entering into combination with other molecules to form addition products.[1]

Similar observations have been made in the case of many other apparently saturated compounds, so that it may be said in general that the affinity represented by single bonds is frequently subject to very considerable variations. This conception may be applied to the solution of diverse problems of general theoretical importance as Siegfried Skraup [2] has recently pointed out.

Ammonium compounds in organic chemistry have been studied in great detail by Werner, and the interpretation of their constitution from the standpoint of his theory may be considered at this point. Ammonium chloride, according to Werner, has neither the formula $NH_3 \cdot HCl$ (molecular formula) nor the formula NH_4Cl (valence formula), but must be regarded as built up in the following way: both ammonia and hydrochloric acid possess auxiliary valencies, the former on the nitrogen, the latter upon the hydrogen atom; and the union of

[1] Ber., **39**, 1284 (1905).

[2] Annalen der Chemie, **419**, 1 (1919), also see Dissertation, Würzburg, 1919.

their molecules to form ammonium chloride is accompanied by the neutralization of these valencies. Thus:

$$H_3N \ldots + \ldots HCl = H_3N \ldots HCl$$

A study of the product shows that the properties of the chlorine present in it differ in no important way from the properties of the chlorine ion in hydrochloric acid; and from this it follows that the union between chlorine and hydrogen must be similar in the two cases. Hydrogen, on the other hand, is seen to have lost its ionic properties as the result of the change. Such a compound of the higher order is referred to by Werner as an addition product ("Anlagerungsverbindung") and belongs to a class of ammonium compounds which must be sharply differentiated from a second class, namely the alkyl ammonium salts.

The hydriodide of methylamine, which results from the interaction of methyliodide and ammonia, may be taken as a typical illustration of an alkyl-ammonium salt. The carbon atom in methyliodide must be regarded, according to Werner's theory, as coordinately saturated, and from this it follows that combination with ammonia takes place as a result of the displacement of one of the atoms occupying a coordinate position. The change in the properties of iodine as a result of this reaction leads to the assumption that it has been detached in some way from its original position with reference to carbon. For example, the iodine might shift its position from carbon to pentavalent nitrogen as is expressed in the following equation:

$$\begin{array}{l} H_3C \cdot I + N = H_3C \cdot NI \\ \qquad\quad H_3 \qquad\quad H_3 \end{array}$$

According to Werner, such an assumption is both capricious and false and should be discarded. He explains the reaction as follows: in this transformation the iodine atom continues to remain in union with the central carbon atom even after its removal from a coordinate position with reference to the latter. This conception supposes that the saturation of the affinity of iodine takes place outside the first sphere of the carbon, since the intrusion of nitrogen has filled all four coordinate positions within the first sphere. According to this interpretation the reaction is to be formulated as follows:

$$H_3CI + NH_3 = I(H_3C \ldots NH_3)$$

The elements or groups directly attached to the central atom whether by principal or auxiliary valencies, and represented as in the first

zone, are included within brackets. The position of the halogen outside the brackets is intended to indicate a difference in its attachment to the central atom, and to show a tendency to ionization in solution. This latter property is possessed in common by all atoms or groups occupying positions in the second or " dissociable zone."

All salt-like derivatives of organic bases (ammonium, phosphonium, arsonium and thionium salts) may be formulated in an analogous manner, as for example:

$$X(H_3C \ldots NR_3); \quad X(H_3C \ldots PR_3);$$
$$X(H_3C \ldots AsR_3); \quad X(H_3C \ldots SR_3)$$

Werner calls compounds of this type intra-addition products (" Einlagerungsverbindungen"), since their configuration presupposes a change in the position of a nitrogen, phosphorus, or other atom from the outer to the inner sphere of the central atom. Werner assumes, further, that under certain conditions it is possible for compounds of this type to rearrange to form normal addition products.

In other words, a tautomeric relation may be imagined to exist between these two classes of compounds as is expressed below:

$$I(H_3C \ldots \underset{\displaystyle H}{NH_2}) \rightleftarrows H_3C{-}\underset{\displaystyle HI}{NH_2}$$

Carbonium form — Hydronium form

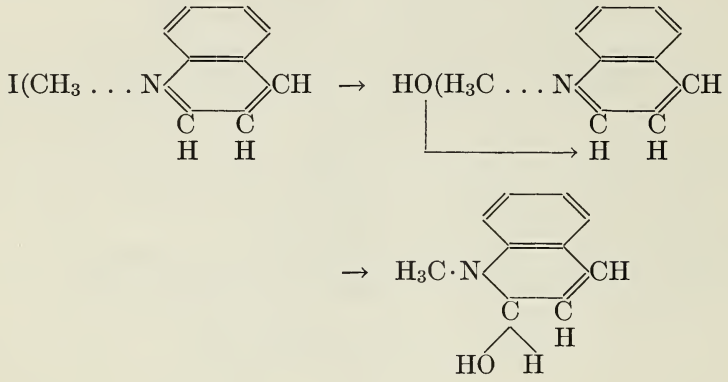
and analogously:

$$HO(H_3C \ldots \underset{\displaystyle H}{NH_2}) \rightleftarrows H_3C{-}\underset{\displaystyle HOH}{NH_2}$$

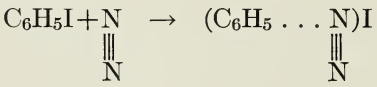
It is possible that in many instances isomers of this type are present in solutions. In the case of tetra-alkyl ammonium compounds, however, isomerism is obviously out of question and these substances are, therefore, assumed to possess the carbonium structure.

The salts of quaternary unsaturated bases represent two important classes of compounds, which may be more clearly understood when their structure is interpreted in the terms of Werner's theory. The salts of the quaternary unsaturated bases include all compounds which are analogous in constitution to the alkyl quinolonium salts and to the salts of the basic dyes derived from triphenylmethane. Substances of this type are not capable of being transformed into stable ammonium bases. When such combinations are hydrolyzed into the corresponding bases they suffer an intramolecular rearrangement which involves a shifting of the hydroxyl group from nitrogen to carbon and the

formation of products which very closely resemble the hydronium compounds. Werner explains this reaction as follows: "the carbon atom adjoining the nitrogen in these compounds has one free coordinate position. The salt reacts to give primarily a base of the carbonium type which then suffers rearrangement. In this process the hydroxyl group shifts from its original position to the free coordinate position on the carbon and thus enters into direct union with this element. This is accompanied by a simultaneous readjustment of affinity relations in the molecule. The reaction may be represented thus:



The same general scheme holds for analogous rearrangements which take place in the case of the basic derivatives of triphenylmethane. In regard to diazonium salts, Werner makes this statement:[1] "the analogy which exists between the theory of the formation of diazonium salts and the theory of the formation of methyl ammonium iodide from methyliodide and ammonia is suggested by the following expression:



A study of the above formulas reveals the interesting fact that, although the carbon atom in union with iodine in phenyliodide is represented as in combination with only three atoms and therefore must be regarded as coordinately unsaturated, it actually behaves like a coordinately saturated atom. This behavior must be due to the constitution of the benzene ring. It follows from a consideration of space relationships that the saturation of a fourth coordinate

[1] Annalen der Chemie, **322**, 290 (1902).

position in the case of any single carbon atom would weaken the affinity by which the ring is held together and in this way destroy the aromatic character of the ring system. The behavior of carbon atoms in aromatic rings differs markedly from the behavior of aliphatic carbon, and is characterized in particular by the fact that the atoms thus bound together in a ring are unable to enter into indirect forms of combination with atoms or radicals outside the ring. Thus the nature of the union of the carbon atoms in aromatic compounds sets a definite stamp upon the character of the coordination formulas of diazonium salts, and also of salts of aniline and of iodonium salts. This may be summed up by saying that the negative radical, which is joined to a carbon atom in the ring by the saturation of one valency, may be displaced from its position in the first sphere to a position in the second sphere with reference to that carbon, by the interposition of other atoms or groups such as N, I, NH_3, etc., but not by the interposition of hydrogen. The compounds resulting from reactions in the cases mentioned may be formulated as follows:

$$\begin{array}{ccc} (C_6H_5 \ldots N)I, & (C_6H_5 \ldots I)I, & (C_6H_5 \ldots NH_3)I \\ \quad\quad\quad\;\; \| & \quad\quad\quad\;\; | & \\ \quad\quad\quad\;\; N & \quad\quad\quad\;\; C_6H_5 & \end{array}$$

While in the case of the first two compounds these formulas correspond to those which are usually assigned to these substances, their significance from the point of view of valence chemistry is quite different, for they serve to express the strongly marked individual character of this class of bodies as compared with the behavior of ordinary ammonium, phosphonium, sulphonium, etc., derivatives. For example, the great instability of the salts of the aromatic amines, and the similarity of behavior between iodonium and thallium salts finds expression in these formulas.

CHAPTER VI

RECENT THEORIES IN REGARD TO VALENCY

The development of Werner's theory in regard to the mechanism of chemical combinations has opened anew the whole problem as to the nature of valency. While this question is one which cannot readily be settled, it may be said in general that there is a tendency at the present time to interpret valency in terms of electrochemical conceptions. The whole matter is, however, in a state of flux and no explanation which is of universal application has as yet been found. The various theories of valency which have been advanced from time to time have had, nevertheless, a more or less pronounced influence upon the theory of structural organic chemistry, so that their origin and development must now be considered.

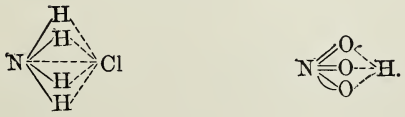
Hugo Kauffmann has recently advanced a theory in regard to the nature of atomic relationships which attempts to express Thiele's and Werner's ideas concerning valency in terms of current electrochemical conceptions. According to Kauffmann, a single valency is to be regarded not as a separate unified force but as made up of a bundle of force lines. If the lines of force which constitute such a bundle are distributed among a number of different atoms, this fact is represented by as many lines as there are valency parts. Valency is then said to be dispersed (" zersplittert "). If, on the other hand, all of the lines of force which roughly correspond to a unit valency are used to hold but one other atom, this fact is represented by a single line or bond. This is equivalent in all essentials to the sign which is commonly employed to represent the current conception of unit valencies, except that it cannot be regarded as of uniform strength, since Kauffmann's theory supposes that the strength of the single bonds which operate between chemical atoms varies greatly under different conditions. In any given instance, the strength of valency may be measured by the relative number of force lines which constitute a bundle.

A system of valency lines is assumed to radiate into space in much the same way as in the case of electric lines of force, and the space which they fill is, therefore, referred to as a *valence field.* Such a

valence field may become an electric field if the course of the valence lines is interrupted by the interposition of electrons.[1] The valence fields which are thus assumed to be present on every molecule are represented in the same way as other force fields, namely, by means of arching lines which extend out into the surrounding space. It follows that the relative amount of space which is occupied by a given valence field will correspond roughly to the relative outside diameter of the bundle of valence lines which constitute it. This conception is in agreement with the observed fact that molecules which contain double bonds have relatively greater molecular volumes than those which contain single bonds. The arch, which is formed by the junction of valence lines radiating from definite positions on the surfaces of each of the two different atoms, must be regarded as corresponding to a condition of tension similar to that in a bent spring. This tension will obviously depend upon the relative curve of the arch, or, in other words, it will vary in proportion to the extent of the valence field. Kauffmann assumes that such points of strain in a molecule are simultaneously points of increased chemical reactivity. The relatively great chemical activity of atoms which are in union by means of double bonds is, therefore, explained as due to tension in the valence field which results from this union. The tension is relieved by breaking the arch in those outermost regions where the strain is greatest. The affinity which is set free in this way then acts to hold new atoms or groups.

According to this conception, partial valencies represent varying fractions of valency and are to be distinguished from principal valencies only by the fact that they are appreciably weaker. Changes in the valency of a given element are interpreted as due merely to changes in the distribution of the total affinity of its atom.

Ionization is supposed to be due to the same general cause, resulting in a particular condition of valence dispersion. The following formulas have, for example, been advanced to explain the ionization of ammonium chloride and nitric acid:



Kauffmann's theory has found its most important application in connection with the development of conceptions which are embodied in the Auxochrome theory and it will, therefore, be referred to again

[1] " Die Valenzlehre," p. 531.

in a later chapter which deals with the relation between color and constitution in organic compounds.

The hypothesis which O. Hinsberg has developed in regard to valency centers in the atoms should be mentioned in this connection but can only be referred to in passing,[1] since lack of space in the present volume prevents its detailed consideration.

Finally, the theory of J. Stark must be considered. This theory differs from those which have just been discussed in that it seeks to connect absorption phenomena in organic chemistry with certain fundamental physical assumptions which underlie the electromagnetic theory of light. Stark points out that while chemists have been content with the assumption that material bodies are built up from indivisible particles called atoms, physicists, on the other hand, have long held the view that the atoms are themselves composite bodies. This conclusion was first arrived at as a result of observations obtained in the spectral analysis of the emanations of radioactive bodies. Further study of radioactive substances led to the formulation of an hypothesis in regard to the direct disintegration of the atom, which received immediate verification and which resulted, among other things, in the formulation of the following general assumptions:

1. The chemical elements disintegrate to give minute particles, which, whatever their source, are alike in that each possesses a mass equal to 1/1700 that of a hydrogen atom, and carries a negative electric charge equal to 4.7×10^{-10} electrostatic units. The minute electrified particles are called *electrons*, and when formed from the various elements are not only identical in mass but carry identical electrical charges.

2. The residue, which is left after one or more electrons have been split off from a chemical atom, is found to possess an equivalent positive charge (positive ion). The mass of such a positively charged particle belongs to the same mathematical order of magnitude as does that of an atom. So far it has not been possible to separate the positive charge on this particle without destroying the integrity of the whole individual. It follows that the positive ions formed from different chemical atoms are different. In other words, while the most varied chemical individuals all give rise to one and the same kind of negative electrons, they do not give identical positive quanta.

The assumption that the chemical atom is composed of a positively charged nucleus and of an electron in union with it does not preclude the possibility that the positive residues are themselves built up of electrons, but as yet there is no positive assurance as to whether

[1] Jour. prakt. Chemie, **93**, 302; **94**, 179 (1916); **95**, 121; **96**, 166 (1917); **98**, 145 (1918); **99**, 232 (1919); Ber., **52**, 26 (1919).

this is, or is not, the case. According to Stark [1] the positive charge of an ion is not distributed uniformly through the particle but is located at that particular point on the atom from which the electron was discharged. The positive and negative quanta that thus constitute a chemical atom must be imagined as in combination with each other not only on the upper surface of the atom but also in the interior of the atom, and it must be assumed, further, that the separation of any single electric quantum from this state of combination results in the formation of positive and negative ions.

Stark assumes that the electric quanta have a certain freedom of motion inside the space defined by the atom, and that these movements correspond to currents (electric fields), which in turn give rise to corresponding magnetic fields. But while electric and magnetic forces must thus be imagined as operating on the upper surfaces of the atoms, the latter must be regarded as insignificant as compared with the former, so far as may be judged from observations up to the present time. Though the part played by the magnetic forces in the attraction and binding together of atoms is slight, it is, nevertheless, not impossible that these forces act in conjunction with electric forces. Stark calculates, further, that forces of gravity are so small as to be negligible when compared with other forces operating between atoms.

A close study by chemists and physicists of the association of atoms indicates that the chemical atoms do not interpenetrate in their combinations, but are bound together mainly by their outer surfaces. It is supposed that the surface of a chemical atom may be adequately represented by a three-dimensional arrangement of positive and negative electrical charges. If the great difference in size between the fundamental units of positive and negative electricity is considered, the surface of the atom must be pictured as made up of extended zones of positive electricity, and between or even above these the comparatively small point-like negative electrons.[2] Since lines of force radiate from the electrons to the positive quanta on the atom, the upper surfaces of the latter may be regarded as constituting an electric field.

Different kinds of atoms differ not only in the number of valence electrons but also in the distance of these electrons from the upper

[1] Jahrb. der Radioaktivität und Elektronik **5**, 124 (1908); **6**, 12 (1909); **9**, 15 (1912); Physikal. Zeitschr., **9**. 85; H. Ley, "Farbe und Konstitution," 68 and 103 (1911), also J. Stark "Die Atomionen chemischer Elemente und ihre Kanalstrahlenspektra," Berlin 1913; "Elektrische Spektralanalyse chemischen Atome," Leipzig, 1914; "Die Elektrizität in chemischen Atom," Leipzig, 1915.

[2] Compare Rutherford and Bohr, Phil. Mag., **21**, 669 (1912); **25**, 10 (1913); and volumes **26** to **30**; also L. Zehnder, "Ueber den Atombau," Verhandl. der Deutschen Phys. Ges., 1916, 324.

surface of the atom, the extension of the lines of force radiating from them, the extension of the positively charged zones on the atom, etc. It also follows that one and the same atom may possess electrons located at different distances from the center of the atom and corresponding positive zones of varying extensions.

If an electron on the upper surface of a chemical atom is at rest it follows that the resultant of all the forces acting upon it must be zero and, further, if it is displaced from this position work must be done. For example, if an electron is imagined as removed from its position of rest by the action of a force at right angles to the axis of symmetry of its field of force, it will simultaneously tend to be pulled back into its original position by the development of an equal force acting in the opposite direction, although it is also conceivable that an electron might move over the whole upper surface of its atom without the development of any resistance. If the electron is removed to a greater and greater distance from its atom, the resistance to be overcome gradually decreases until a limit is reached when the resistance is equal to zero and when the electron separates completely from its atom.

According to Stark, atoms are much more variable in constitution than has previously been supposed, since every displacement of an electron from its position of rest is attended by fundamental changes in its electric field. These effects extend below the surface of the atom, since changes in the position and extension of the positive zones must produce simultaneous internal changes. Thus each position of a valence electron corresponds to a definite condition of the atom as a whole, or in other words, a condition of equilibrium exists between the electron and its atom. If, however, an electron is displaced from its position of rest, as, for example, by the chemical action of another atom, the equilibrium in the system representing the relation of the electron to its atom is destroyed.

Negative electrons located on the upper surfaces of the atoms may, according to Stark, be regarded as *valence electrons*, since they serve to bind one atom to another and therefore perform the same functions as have in the past been attributed to valency. In terms of Stark's theory the valency of a chemical element corresponds to the number of electrons which are present on the upper surfaces of its atoms. Combinations between atoms result from the attractions exercised by the positive zones of one atom for electrons located on the upper surfaces of others. Moreover, since the structure of an electric field is usually represented by the course and density of the lines of force which originate at positive charges and end at equally great negative

charges, we must imagine a system of lines of force radiating in all directions from the point-like negative electrons and terminating in the extended positive zones. The point-like origin and the diverging course of the lines of force are important facts to be remembered in considering the union between one atom and another, since disparity in the size of the positive and negative units of electricity must be regarded as the determining factors in establishing simple relationships between atoms.

Stark divides chemical atoms into three general classes, namely electro-positive, electro-negative and electro-dual ("electrozwiefach"). For example, an atom, or, in other words, the valence field of an atom, may be regarded as electro-positive in character when its electron is situated at a distance from the atom equal to or greater than the diameter of the atom. Fig. 1 represents diagrammatically a sector of a positive valence field in a plane which cuts both the atom and its electron. The figure also indicates the extension of the field in which the electron may be regarded as at rest with reference to its atom.

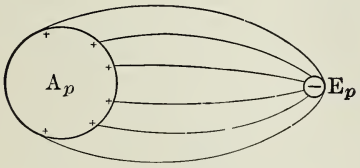


Fig. 1.

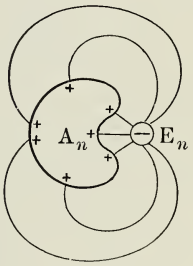


Fig. 2.

The picture presented by a negative valence field is quite different, as Fig. 2 shows. Here the valence electron is represented as in close proximity to the surface of its atom. The indentation serves to show that the free movement of the electron is limited and that the field in which it may be regarded as at rest with reference to its atom is much contracted and almost point-like as compared to that shown in Fig. 1. The lines of force which radiate from the electron to the positive zone on the surface of the atom are represented as strongly deflected, and the electric field which they cover is, therefore, much more extensive than in the case of an electro-positive atom.

Electro-positive and electro-negative atoms differ in their ability to combine with the negative electrons of other atoms and thus to enter into various forms of chemical combination. Electro-positive atoms, for example, are so fully engaged in holding the valence electrons which

properly belong to them that they may be assumed to have very little free affinity with which to attract and hold the electrons of other atoms. Under these circumstances chemical combination with other atoms is brought about by the action of the negative electrons. In other words, the union of electro-positive atoms with other atoms results from the saturation of lines of force emanating from their electrons rather than from the positive zones of the atoms themselves. Electro-negative atoms, on the other hand, possess the power to attract and hold a greater number of electrons than properly belong to them and they are, therefore, capable of entering into chemical relationships with other atoms through the saturation of lines of force emanating from the positive zones of their atoms. It follows that chemical combination between electro-positive and electro-negative atoms results from the saturation of lines of force emanating from negative electrons attached to the electro-positive atoms and terminating in positive zones on the surfaces of the electro-negative atoms.[1]

Electro-dual atoms are assumed by Stark to be more or less intermediate in structure between electro-positive and electro-negative atoms. They resemble the latter in that the free movement of their valence electrons is restricted. In other words, the field in which the electron is at rest with reference to its atom is contracted and almost point-like in extent. They differ from electro-negative atoms in that their electrons are subject to less strain as the result of displacements from their normal positions of rest to other positions perpendicular to the axes of the atom at successive points and equidistant from the center. Electro-dual atoms differ from electro-positive atoms in that their positive zones possess greater power to hold the electrons of other atoms. This power is, however, less than that of electro-negative atoms.

Atoms may be assumed to differ not only in the structure of their valence fields but in the number of these fields. They may, therefore, be classified as mono-, di-, or tri-polar, according to the number of valence electrons which they possess. Carbon atoms may be regarded as having four electrons of the electro-dual type, nitrogen and phosphorus, three; and oxygen and sulphur, two. Halogens, on the other hand, are unipolar and represent the most pronounced type of electro-negative atoms.

In all cases, chemical action is due to the saturation of lines of force emanating from the valence electrons of one atom and terminating in the positive zones of another. In the simplest type of combination an electron is bound to only one other atom besides its own, but since

[1] "Die Elektrizität in Chemischen Atom," p. 71.

the atoms of different elements are characterized by the presence of one, two, three or more electrons, this condition may obviously be duplicated on a given atom. Under these circumstances the atoms in question are said to be bound together by means of double or triple bonds. Such a condition must be sharply distinguished from so-called multiple unions where the lines of force from a given electron terminate in the positive zones of two or more atoms besides its own.

In the union of two atoms by means of single bonds a number of typical arrangements may be postulated. For example, the combination of two electro-negative atoms may be assumed to take place as represented in Figs. 3*a* and 3*b*, while that of two electro-positive atoms is shown in Fig. 4.

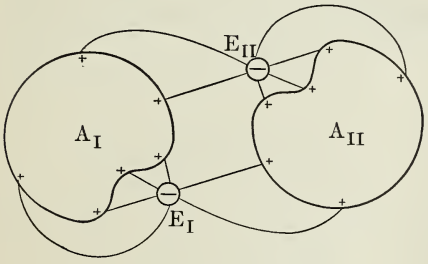


FIG. 3*a*.

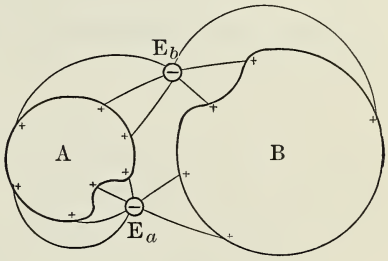


FIG. 3*b*.

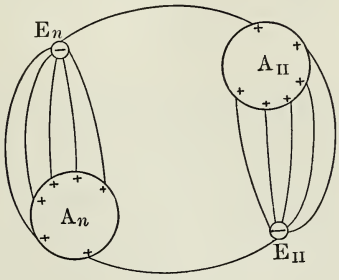


FIG. 4.

In both instances the union of the two atoms is supposed to be accompanied by only a very slight contraction of their respective fields of force and, therefore, represents at best a weak form of chemical combination. The union between two electro-positive atoms may be assumed to be even weaker than in the case of electro-negative atoms, since the former have actually been observed to exist in monoatomic condition in the gaseous state. Reactions between electro-positive and electro-negative atoms must be considered in somewhat greater

detail. Fig. 5 represents such a union and shows that the electro-negative atom A_n has attracted the valence electron E_p of the electro-positive atom A_p to a position which is nearer to its circumference than that of its own electron E_n. The atom A_p and the system E_p–A_n–E_n thus appear to revolve upon a common axis. If an outside force now acts upon both atoms in such a way as to tend to separate them from each other, the effect will be to change the relative distance of E_p from A_p more rapidly than that of E_p from A_n. If the disturbing influence is sufficiently great to overcome the resistance offered by the attraction operating between A_p and E_p, the electron may become separated from its own atom while still continuing to be bound to the stronger atom. Such a condition would result in the dissociation of the compound A_p–A_n into positive and negative ions, corresponding respectively to A_p and the system E_p–A_n–E_n.

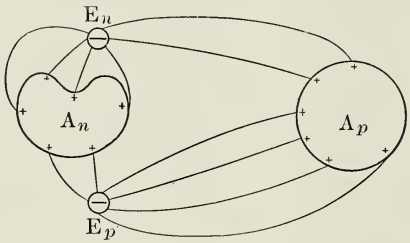


Fig. 5.

Combinations of so-called electro-dual atoms with each other or with electro-positive or electro-negative atoms take place with only minor modifications of this general scheme. In visualizing these relationships it is, however, necessary to remember that the valence electrons of electro-dual atoms occupy positions somewhat further away from the surfaces of their atoms than in the case of electro-negative atoms. Moreover, while such an electron may be assumed to possess a definite position of rest with reference to its free atom, it may, as a consequence of the chemical combination of this atom, become displaced from this position without the immediate development of strain. Carbon and hydrogen represent examples of atoms of this type and may be imagined as entering into chemical combinations through the exercise of single bonds according to the following scheme (Fig. 6). While a carbon atom may be assumed to possess four valence electrons arranged above its surface in positions which correspond roughly to the four corners of a tetrahedron, the above

diagram serves to represent only a single sector of the atom and shows but one of its four poles.

In the combination of two carbon atoms the valence electrons may be assumed to have suffered displacement from their original positions of rest with reference to their free atoms, with the result that each electron is bound to both atoms. The union of E_I to C_{II} is, however, relatively weaker than the union of E_I to C_I so that dissolution of the compound takes place without ionization. It is to be noted further that the valence fields E_I–C_I and E_I–C_{II} resemble each other much more closely than the valence fields E_p–A_p and E_p–A_n and that the former arrangement may, therefore, be regarded as representing relatively the strongest type of union between chemical atoms. These considerations taken in conjunction with the assumption of the tetravalence of carbon serve to account for the number and variety of hydrocarbons [1] and also for the fact that such compounds do not undergo electrolytic dissociation.

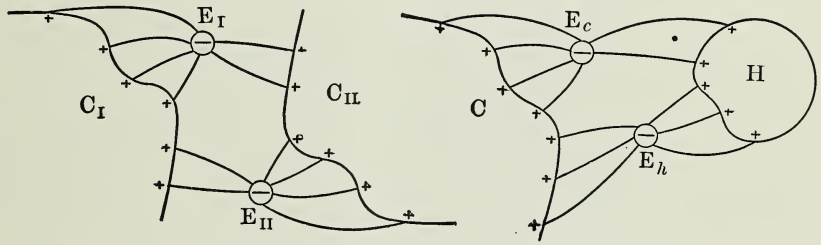


Fig. 6.

If an electro-dual atom (A_z) enters into chemical combination with an electro-negative atom, the resulting valence fields will closely resemble those which have just been described in connection with the union of two electro-dual atoms. Since, however, E_z may be assumed to possess relatively great elasticity as regards the limits of its displacement with reference to its own atom, it is free to respond to the attraction of A_n without weakening its relation to its own atom. In the union of two such atoms E_n is simultaneously drawn to A_z, but since the valence field E_n–A_z represents a relatively small attractive force distributed over a relatively great area, it forms the weakest part of the union between the two atoms. It may, therefore, be assumed to offer the least resistance to the action of an outside force and, in opening, to afford points of attraction for an adding molecule. Such a conception serves to account for the mechanism of the formation of addition products or, in general, of all so-called molecular compounds.

[1] " Die Elektrizität in Chemischen Atom," p. 82.

The combination of an electro-dual and an electro-positive atom is attended by the expenditure of very little energy. Such unions may be fairly stable, as in the case of the metallic carbides. In the case of zinc methyl on the other hand, and in the case of those metallic derivatives of the hydrocarbons which have been described by Schlenk, this type of combination appears to be distinctly unstable. The latter compounds are especially sensitive to the action of non-metals, under the influence of which the valence field E_z–A_p opens, and thus affords an opportunity for the union of A_p with the electro-negative atom.

Two atoms may enter into combination by means of so-called double bonds if four electrons—two for each atom—are free to engage in establishing the union. In visualizing such an arrangement it must be assumed that the two pairs of valence fields lie in different planes. Figs. 7*a* and 7*b* represent sections of two doubly-bound carbon atoms which are supposed to lie at right angles to each other:

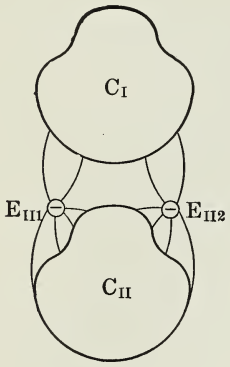


Fig. 7*a*.

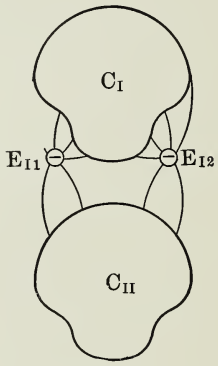


Fig. 7*b*.

The valence electron of one atom is thus imagined as sending lines of force to positive zones which lie between two valence electrons of the second atom. It is obvious that atoms which are bound together in this way are not, like singly-bound atoms, free to rotate about a common axis. If, for example, the atom C_I (represented in Fig. 7*a*), were to rotate about the axis of symmetry of its valence field while C_{II} remained motionless, the effect would be to bring the valence electrons of C_I nearer to those of C_{II}. Such a movement would involve a lengthening of the fields of force between C_I and its electrons since only in this way would the latter be enabled to pass outside the force fields of C_{II} and its electrons. Since, however, any force tending to

separate an electron from its position of rest with reference to its own atom is always met by an equally great resistance, a torsion in the opposite direction should act simultaneously to bring C_I back to its original position with reference to C_{II}. The fact that freedom of movement of C_I with reference to C_{II} is obviously impossible under these conditions serves to account for the phenomenon of stereo-isomerism which has been observed in the case of fumaric and maleic acids and other substances of the general formula:

$$\begin{matrix} R_1CR_2 \\ \| \\ R_3CR_4 \end{matrix} \quad \text{and} \quad \begin{matrix} R_2CR_1 \\ \| \\ R_3CR_4 \end{matrix}$$

Double bonds may be assumed to open more readily than single bonds under the action of an outside force and, in so doing to afford points of free affinity within the molecule. This conception serves to account for the ease with which substances containing doubly bound atoms react to form addition products, polymerization products and molecular compounds.

The usual method of representing unsaturated linkages by means of double bonds is retained by Pauly and Stark, but, according to the terms of Stark's theory, must be regarded as indicating merely a normal and stable mean condition. . Such a condition is possible only when the two carbon atoms are symmetrically arranged and when the molecule is itself in a condition of rest and unacted upon by outside forces.[1]

The earlier papers published by Stark interpreted the phenomenon of unsaturation in quite a different manner from that which has just been described, and assumed that the two unsaturated atoms were held together by means of a single bond and that each was characterized by the presence of a free (" gelockert ") valence electron. While the development of this portion of Stark's theory has been omitted from the present edition [2] it must, nevertheless, be conceded that this conception has been the basis for a satisfactory interpretation of certain reactions which are inexplicable in terms of any of the other theories. Thus, for example, H. Pauly,[3] in conjunction with von Buttlar, has been able to demonstrate experimentally that phenolic aldehydes are markedly less reactive than other aldehydes. This is shown in the fact that benzoin condensations, intramolecular oxidations and reductions in the presence of alkali (Cannizzaro), the formation of hydrox-

[1] Ber., **48**, 2017 (1915).

[2] Compare 1913 Edition.

[3] Annalen der Chemie, **383**, 230, 288 (1911); Ber., **48**, 2010 (1915); Jour. prakt. Chemie, **98**, 106 (1918).

amic acids (Angeli), the reaction with ortho-formic esters (Claisen), acetalization with alcohol and hydrochloric acid (E. Fischer), the naphthoquinone-carboxylic acid reaction (Doebner) and finally the fuchsine-sulphuric acid reaction, all take place less readily in the case of hydroxy-aldehydes than in the case of unsubstituted aldehydes, and in certain instances it may even happen that the normal course of the reaction is definitely interfered with as a result of the introduction of the hydroxyl group. It has, moreover, been established by these investigators that the phenolic oxygen as a whole is the determining factor in influencing these reactions.

Pauly has been unable to explain these phenomena in terms of any of the current theories with the single exception of the electro-atomic theory of Stark. According to Stark's earlier method of representation, the presence of single bonds between atoms is indicated by means of the symbol $\longleftrightarrow$, and free electrons by the symbol $-\circ$. The aldehyde group and the hydroxy-aldehyde group may, therefore, be represented in terms of Stark's theory by means of the diagrams shown respectively in Fig. 8 and Fig. 9. It will be observed that in Fig. 9 the double

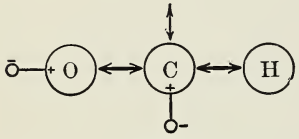


Fig. 8.

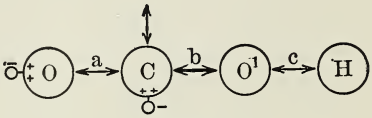


Fig. 9.

arrow, $\overset{b}{\longleftrightarrow}$, between the carbon atom and the hydroxyl group is printed in heavy type. This serves to indicate that the union is relatively a very stable one. The double arrow, $\overset{a}{\longleftrightarrow}$, on the other hand is printed in light type and thus indicates that this form of combination between carbon and oxygen is relatively labile in character. The facts which are here represented may be expressed in terms of Stark's theory by saying that the positive field of force on the aldehyde oxygen atom is not fully occupied in holding the carbon atom ($\overset{a}{\longleftrightarrow}$) and can, therefore, engage its free electron ($-\circ$) with a relatively great fraction of its affinity. Such a condition corresponds to a decrease in the reactivity of the carbonyl. A further study of Fig. 9 shows that the hydrogen atom of the hydroxyl group is in a loose form of combination with oxygen. Such a condition may result in the ionization of the hydrogen under the action of a solvent. In this event the hydrogen atom may be assumed to have lost its negative valence electron and must, therefore, be regarded as bound to the oxygen atom only by those lines of

force which operate between the negative valence electron of the oxygen atom and the positive zone of the hydrogen atom. Such a one-sided type of union is indicated by the single arrow, $\overset{c}{\longrightarrow}$ in Fig. 10. This figure represents diagrammatically an hydroxy-aldehyde after ionization of the hydrogen has occurred;

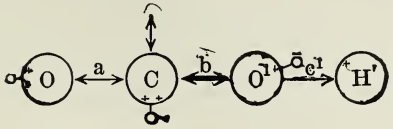


Fig. 10.

Another type of hydroxy aldehyde is shown in Fig. 11:

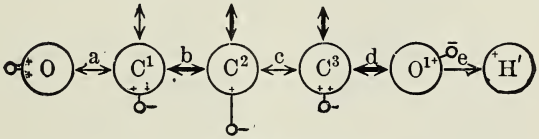


Fig. 11.

Here the strong union represented by the double arrow, $\overset{d}{\longleftrightarrow}$, results not only in the ionization of the hydrogen of the hydroxyl group but also affects other parts of the molecule. The most immediate effect is upon the valence electron on C^3 which is represented as in close contact with its atom, thus indicating that the negative charge of this atom is fully engaged. The union between C^3 and C^2 is simultaneously weakened and this in turn acts to strengthen the linkage $\overset{b}{\longleftrightarrow}$ between C^2 and C^1. The fact that C^1 is thus called upon to exercise a relatively large part of its free affinity in holding C^2 leaves this atom with relatively little affinity for its union with oxygen. The latter is thus able to engage its free ("gelockert") valence electron more energetically and the latter moves to a position near the surface of the atom. As in the preceding case this condition is reflected in a decrease in the reactivity of the carbonyl group. Both illustrations not only serve to show how a change in the relative strength of the union between two atoms in a molecule is inevitably accompanied by simultaneous changes in other parts of the molecule, but also help to support Stark's general theory that no linkage can be strengthened except at the expense of another. In the light of this theory it is easy to understand how the introduction of a given substituent into a chain of carbon atoms or into a ring compound may come to have an important

influence upon the reactivity of other atoms or groups even when these are located in a distant part of the molecule.[1]

When two atoms unite by means of triple bonds, six valence electrons are engaged, three for each atom. In this case Stark, in his recent treatises, assumes that all three electrons belonging to a given atom lie in the same plane, and that the two planes represented by the two sets of electrons are parallel to each other but at some distance apart. The union of two nitrogen atoms by means of triple bonds, N≡N, is shown in Fig. 12*a*, and Fig. 12*b*.

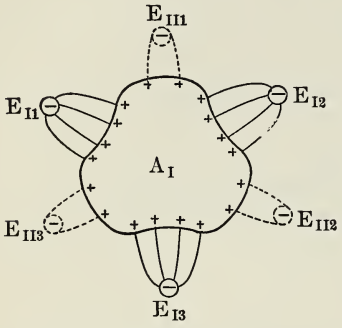


Fig. 12*a*.

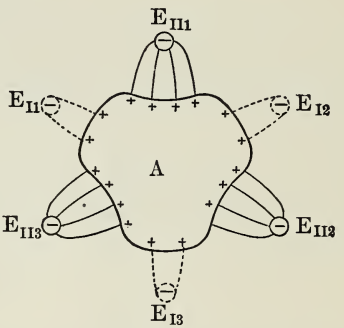


Fig. 12*b*.

Here each figure represents a section taken in such a way as to cut the three valence electrons as well as the positive zones of each atom. Since the two sections lie in different planes, one above the other and at some distance apart, they obviously cannot be represented in the same drawing although the relative positions of the electrons of the second atom with reference to the positive zones of the first may be indicated in each case by means of dotted projections. As in the case of doubly-bound atoms, free rotation of the atoms is obviously impossible. A consideration of the fields of force leads to the conclusion that this form of combination is less stable than in the case of single bonds but that it is less sensitive to the action of an outside force than in the case of double bonds.

Stark has attempted to deduce the properties of a large number of chemical compounds from a consideration of the force fields in atomic groupings such as N=N, C≡N, CH_3, NH_2OH, etc., and, as a result, has been able to demonstrate that many of the variations in the chemical relationships of the atoms which the older theories of valency have failed to elucidate, may be accounted for readily in terms of his theory. His system serves to explain the most varied phenomena

[1] Compare Meerwein, Annalen der Chemie, **419**, 121 (1919).

in inorganic as well as in organic chemistry, such as changing valency, intermolecular combinations, etc.

It may be added that H. Pauly represents the various types of union between atoms by means of symbols which possess the advantage of being simpler than those which have been suggested by Stark:

Types of Electro-valency	According to J. Stark	According to H. Pauly
1. Ionic	O→H	O→H
2. Simple linkages	C⇄C	C—C
3. Double linkages (benzene)	C⇄C	C⌒C
4. Double linkages (olefine)	C⇄C	C═C
5. Acetylene linkages	C⇄C	C≡C

It should be noted, however, that in the case of Pauly's symbols a single line is always understood to represent the saturation of two valence electrons.

Among the more recent interpretations which have been advanced to explain the various relationships which exist between the atoms, must be mentioned the kineto-electro-magnetic theory of J. Beckenkamp[1] and the kinetic theory of A. von Weinberg.[2] Neither of these theories can, however, be more than referred to at this time.

In conclusion it may be said that Stark's theory in regard to atomic relationships is of especial interest to chemists because of the fact that it seeks to establish a relation between the structure of different valence fields and the optical properties of the substances in which they are found. In this connection it may be said briefly that the valence fields of the atoms present in the molecules of chemical elements and compounds are assumed to vibrate between definite positions of equilibrium, and that these movements are electro-magnetic in character and are accompanied by the emission and absorption of light. The waves of light which are emitted or absorbed by a particular valence field are assumed, moreover, to possess the same frequency as the valence field itself, so that by measuring the frequency

[1] Verhandl. d. Phys. Med. Geo. zu Würzburg, **45**, 135 (1918); "Leitfaden der Krystallographie," by J. Beckenkamp, p. 387 and following. Pub. by Bornsträger, Berlin, 1919.

[2] Ber., **52**, 928 and 1501 (1919).

or intensity of these waves of light it is possible to determine the character of the valence field and thus to arrive at certain definite conclusions in regard to the nature and strength of union of valence electrons in their positions of equilibrium. The constitution of the molecule may in this way be deduced from a study of the optics of its respective valence fields.

Stark's theory, thus briefly outlined, represents in its fundamental aspects a resurrection of the electrochemical theory of Berzelius. Stark's particular contribution consists in bringing the more fundamental electrochemical conceptions into harmony with modern physical ideas in the field of atomicity, and in this way developing a much broader interpretation of the mechanism of chemical action than is possible in terms of the prevailing theory of valency. Stark's conceptions allow of a much more intimate understanding of the chemical relationships of the atoms than is otherwise possible and at the same time, they anticipate much finer differences in structure than is afforded by the application of any other single theory. On the other hand, it cannot be denied that these conceptions are somewhat involved and do not lend themselves easily to any brief summary. Stark himself acknowledges [1] that—" many chemists may be dismayed by the profusion of different images which may be derived from our valence hypothesis, may regard it as intricate, and may even hesitate to penetrate into the labyrinth of types of chemical combination which we have described." Nevertheless, Stark's theory is as comprehensive as any current at the present time. In that it attempts to explain in terms of modern physical conceptions the relation which has been observed to exist between the optical properties of a substance and the chemical constitution of its molecule, it serves to combine the interest of both physicists and chemists upon the solution of a problem which offers the most promising developments of any now under investigation.

[1] " Die Elektrizität in chemischen Atom," p. 94.

CHAPTER VII

THE ELECTRON CONCEPTION OF VALENCY

On the basis of the electron theory, Falk and Nelson [1] have developed a set of conceptions which embody J. J. Thomson's ideas [2] regarding the constitution of the atom. They start with the assumption that each individual atom represents a close confederation of electrons, or, as J. J. Thomson calls them, "corpuscles," and that these are in constant motion. If, by the action of physical or chemical forces, one or more electrons are separated from the atom, the latter receives a corresponding positive charge. Since such a positive charge acts as an attractive force in holding electrons together in the molecule, it follows that the number of electrons which may be separated in this way is very small.

The atoms of the different elements differ from each other in the ease with which their electrons dissociate. According to Thomson, certain atoms have also the power to combine with free electrons and, in so doing, to receive a negative electric charge. Such atoms differ both as to the ease with which they add electrons and in their ability to hold the electrons which have been added. Elements whose atoms behave in this way are called electro-negative in contradistinction to the electro-positive elements whose atoms tend to lose electrons and so to receive a positive charge.

If the affinity of the elements for each other is electrical in character it follows that the ability of an atom to enter into chemical combinations will depend upon its power to hold an electric charge. In terms of this theory, a monovalent atom is one which carries a unit charge of electricity, while a multivalent atom is one which bears two or more such units, the number varying according to the valency of the element.

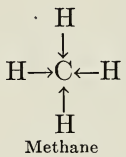
Every chemical combination between atoms is accompanied by an exchange of electrons—one atom losing an electron and becoming thereby positively charged, and the other atom receiving an electron and becoming negatively charged. To denote this change Thomson

[1] Jour. Am. Chem. Soc., **32**, 1637 (1910).

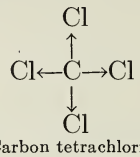
[2] The Corpuscular Theory of Matter, p. 138 (1907).

used the so-called "Faraday Tubes of Force" instead of the usual + and − signs, while Falk and Nelson uses an arrow, →. The direction of the arrow is used to denote the direction taken by the electron in its passage from one atom to the other.

Hydrogen shows by its properties that it is an electro-positive element, or, in other words, that it tends to lose an electron in the process of chemical combination with other atoms. It does not seem to possess the opposite faculty of adding electrons. Carbon, on the other hand, shows from its properties that it possesses the power both to add and to lose electrons; in other words it is both electro-negative and electro-positive in character. This is indicated, in the case of two of its compounds, by means of the following formulas:

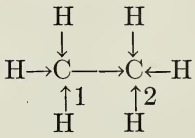


Methane



Carbon tetrachloride

The formula for ethane becomes:



and differs from the ordinary structural formula assigned to ethane in that the carbon atoms 1 and 2 are not alike in all respects, since C_2 possesses one electron more than C_1. Similar relationships are even more strikingly evident in the formulas of other compounds which will be referred to later, and serve to account for the fact, so frequently observed, that one of two apparently identical groups is actually more reactive than the other. The significance of this is brought out most conspicuously in the case of the homologous series of dibasic acids. In the case of this series, a regular increase in the number of carbon atoms is not accompanied by a regular variation in melting point, solubility, etc. A close study of the properties of these substances shows, further, that acids possessing an even number of carbon atoms (as 2, 4, 6, etc.) resemble each other much more closely and regularly than the acids immediately following each other in the series (as 1, 2, 3, etc.). The same general statement holds true for acids having an uneven number of carbon atoms (as 3, 5, 7, etc.).

These facts, which are not accounted for in any way by the ordinary structural formulas of the compounds, may be explained by the electronic formulas of Falk and Nelson. Thus the acids I and II,

$$\underset{\text{I}}{HOOC \leftarrow CH_2 \rightarrow COOH} \quad \text{and} \quad \underset{\text{II}}{HOOC \leftarrow CH_2 \rightarrow CH_2 \rightarrow COOH}$$

show a symmetrical distribution of electrons for acids having an odd number of carbon atoms, and an unsymmetrical distribution of electrons for acids having an even number of carbon atoms. The fact that the symmetrical arrangement alternates with the unsymmetrical arrangement for the series as a whole accounts for the irregularities in properties of acids which immediately follow each other in the series.

Since substituting groups, each in its own characteristic way, affect the mobility of electrons in a given atom, it is necessary to distinguish between two classes of olefines, viz., those in which the two halves of the molecule are similar (as, for example, $R_2C{=}CR_2$ and $RR'C{=}CRR'$) and those in which the two halves are dissimilar (as, $R_2C{=}CRR'$, $R_2C{=}CR_2'$, $R_2C{=}CR'R,''$ etc.).

According to Falk and Nelson, the union of two carbon atoms by means of a double bond involves the transference of two electrons from one carbon atom to the other, and this may take place in either of two ways:

$$R_2C \rightrightarrows CR_2, \quad \text{or} \quad R_2C \leftrightarrows CR_2$$

$$RR^1C \rightrightarrows CRR^1, \quad \text{or} \quad RR^1C \leftrightarrows CRR^1$$

Of the two isomers possible in each case, one must be more stable than the other. Because no isomerism has as yet been discovered in the case of substances belonging to the class represented by $R_2C{=}CR_2$, Falk and Nelson assume that one of the two isomers theoretically possible is so unstable that it is transformed instantly into the other stable form.

Compounds of the general formula $RR'C{=}CRR'$ are commonly found in two isomeric modifications; but according to the present theory three isomers are possible, as for example:

$$CH_3CH \rightleftarrows CHCH_3; \quad CH_3CH \rightrightarrows CHCH_3; \quad \text{and} \quad CH_3CH \leftrightarrows CHCH_3$$

To explain the discrepancy between fact and theory it may be assumed, as in the preceding case, that one of the three possible isomers is so unstable that it cannot be isolated. It may be said, however, that the present lack of harmony between fact and theory in such cases must be regarded as an evidence of weakness in the interpretations of Falk and

Nelson. Similar objections hold in the case of triply bound carbon where a number of isomers are theoretically possible and where only one substance having the formula $RC \rightleftarrows CR$, is assumed to be stable.

Nitrogen has the power to add three electrons as the formula of ammonia shows. That nitrogen has also the power to lose five electrons is obvious from a consideration of its oxygen compounds. Thus the nitrogen in ammonia differs from the nitrogen in nitric acid by eight electrons. The chemical properties of compounds containing nitrogen, in which that element is in simple union with other atoms or groups of atoms, depend upon whether such atoms or groups are electro-positive or electro-negative in relation to nitrogen. For example, Falk and Nelson assume that in hydrazine the following relation exists:

$$H_2 \rightrightarrows \underset{\alpha}{N} \rightarrow \underset{\beta}{N} \leftleftarrows N_2$$

Thus the α-atom is seen to hold one, while the β-atom holds three negative charges, and expression is given to the fact that the two nitrogen atoms are not equivalent. The difference in chemical properties between them is shown, for example, in the ease with which they combine respectively with hydrogen chloride. Thus the dichloride is unstable and readily loses a molecule of hydrochloric acid, so that the hydrazine functions more as a mono- than as a di-acid base. Similar differences are even more strongly marked in the case of derivatives of hydrazine.

Isomeric diazo-compounds are formulated as follows:

$$R \rightarrow N \underset{\downarrow X}{\leftleftarrows} N; \quad R \rightarrow N \leftleftarrows N \rightarrow X; \quad R \rightarrow N \rightleftarrows N \rightarrow O \leftarrow H$$

Diazonium salt — Syn-diazo compound — Anti-diazo compound

If the atoms of different elements are in simple forms of combination, it is usually possible to predict, from the nature of the elements in question, the direction in which the electron of a given atom will move. If two atoms are doubly bound, the second electron may move in the same direction as the first or in the opposite direction. In this way three structural isomers may arise, which, of necessity, must differ as to stability. In the case of the carbonyl group, for example, the electrons may be distributed as follows:

$$\underset{\text{I}}{C \rightrightarrows O}; \quad \underset{\text{II}}{C \rightleftarrows O}; \quad \underset{\text{III}}{C \leftleftarrows O}$$

Of these forms, I must be extremely stable, III must be so very unstable that it cannot be isolated, while II represents a mean between I and

III in its properties. The stable and labile forms of benzophenone, which, according to Schaum,[1] differ as to their chemical behavior, may be regarded as representing types I and II respectively.

The well-known isomerism of the aldoximes is regarded by Falk and Nelson as due not to space isomerism but to the following distribution of electrons:

$$\underset{\text{Anti-form}}{RHC \rightrightarrows N \rightarrow O \leftarrow H}, \quad \text{and} \quad \underset{\text{Syn-form}}{RHC \rightleftarrows N \rightarrow O \leftarrow H}$$

The difference in chemical properties shown by the two forms, must, in terms of the present theory, be due to the difference in the union of carbon and nitrogen in the two cases. A similar interpretation holds for the ketoximes. Thus the Beckmann rearrangement depends upon the potential difference between the group which substitutes for OH, and that which contains the nitrogen atoms.

Since the individual parts of a chemical compound, must, in general, bear different charges, it follows that one part of a molecule bearing a positive charge will tend to attract a part of some other molecule which carries an opposite charge. This kind of affinity must differ, both in nature and in intensity, from that which operates by the transfer of an electron to produce simple types of chemical combination. Falk and Nelson assume that it corresponds in character to partial or residual valencies. The electrical attraction exercised by an atom or group of atoms for others in other molecules of the same or of different compounds may give rise to combinations which are sufficiently stable under ordinary conditions to produce the characteristic properties of a new substance, such as, for example, its distinctive color.

Classification of Organic Reactions

According to the electronic conception of chemical change,[2] the phenomena of oxidation, reduction and valency may be briefly defined as follows: *oxidation* of an atom involves the loss of electrons, or the gain of positive charges, while *reduction* is the gain of electrons, or the loss of positive charges. The *valence* of an element is the number of corpuscles (negative electrons) which an atom of that element loses or gains when it enters into chemical combination. Based on the above conceptions, organic reactions (or inorganic reactions) may be classified as follows:

[1] Chem. Zeitung, **47**, 417 (1910).

[2] Nelson, Beans and Falk, Jour. Am. Chem. Soc., **35**, 1810 (1913).

1. Reactions in which the algebraic sum of the positive and negative charges on a definite atom of the molecule changes:

(*a*) The number of electrons increases.
(*b*) The number of electrons decreases.

2. Reactions in which the algebraic sum of the positive and negative charges on the atom remains constant:

(*a*) The arithmetical sum changes.
(*b*) The arithmetical sum remains constant.

Reactions classified under 1*a* and 1*b* are those involving reduction and oxidation respectively. The oxidation and reduction of the atoms of carbon, nitrogen and iron are represented in the following reversible electronic equations:

$$\overset{=\,=}{\underset{=\,=}{C}}H_4 \rightarrow \overset{=\,+}{\underset{=\,=}{C}}H_3Cl \rightarrow \overset{=\,+}{\underset{=\,+}{C}}H_2Cl_2 \rightarrow \overset{=\,+}{\underset{+\,+}{C}}HCl_3 \rightarrow \overset{+\,+}{\underset{+\,+}{C}}Cl_4$$

$$\overset{=\,=}{\underset{=\,=}{C}}H_4 \rightarrow \overset{=\,+}{\underset{=\,=}{C}}H_3OH \rightarrow \overset{=\,+}{\underset{=\,+}{C}}H_2O \rightarrow \overset{=\,+}{\underset{+\,+}{C}}H_2O_2 \rightarrow \overset{+\,+}{\underset{+\,+}{C}}O_2$$

$$\overset{=}{\underset{=\,=}{N}}H_3 \rightarrow \overset{+}{\underset{=\,=}{N}}H_2OH \rightarrow \overset{+}{\underset{=\,+}{N}}H(OH)_2 \rightarrow \overset{+}{\underset{+\,+}{N}}O(OH) \rightarrow \overset{+\,+\,+}{\underset{+\,+}{N}}O_2(OH)$$

$$\overset{+\,+}{Fe}Cl_2 \rightarrow \overset{+\,+\,+}{Fe}Cl_3$$

$$\xrightarrow{\text{Oxidation}}$$

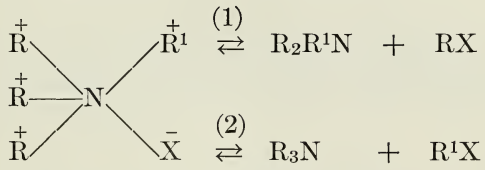
$$\xleftarrow{\text{Reduction}}$$

Reactions characteristic of Class 2*a* are those which Nelson and Falk term the " onium " type. For example, the addition of hydrogen chloride, $\overset{+\,-}{H}Cl$, to ammonia, $\overset{=}{\underset{=\,=}{N}}H_3$, forms ammonium chloride, $\overset{=\,=\,+}{\underset{=\,=}{N}}H_4Cl$, producing thereby an arithmetical increase in electrical charges but no algebraic increase. Other representatives of this group of " onium " compounds are iodonium, $\overset{=\,+\,+\,-}{\underset{=\,=}{I}}R_2X$, sulphonium, $\overset{=\,+\,+\,-}{\underset{=\,=}{S}}R_3X$, and arsonium compounds, $\overset{=\,=\,+\,+\,-}{\underset{=\,=\,=}{As}}RX$. The reverse transformations would also appear in this classification. Some interesting " onium " formations are later discussed in connection with the phenomena of esterification, saponification, etc. Reactions characteristic of Class 2*b* are those represented by the term metathetic, and include all ionic transformations

which do not involve oxidation or reduction. Tautomeric rearrangements are also included here.

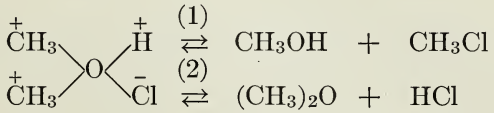
The Significance of "Onium" Compounds in Certain Chemical Reactions [1]

The addition of alkyl halides to amines with formation of quaternary ammonium salts is a reversible reaction, dissociation being favored by rise of temperature and the action of alkali. These transformations lead to two types of equilibria when more than one alkyl group is present, and the change which predominates is that

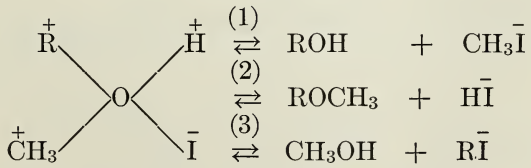


one which proceeds with the greatest velocity, or in which one or more of the products formed is removed from the sphere of reaction. The addition product or quaternary salt is an "onium" compound of nitrogen.

Dimethyl ether and hydrogen chloride combine at a low temperature to form an addition product, or oxonium salt, which is extremely unstable. A rise in temperature leads to dissociation of the onium compound, and equation 2 represents the equilibrium which predominates.



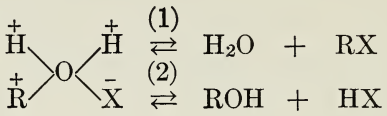
The well-known Zeisel method for the determination of methoxy groups is a practical illustration of this phenomenon, and in terms of the "onium" theory the reaction may be formulated as follows:



[1] Falk and Nelson, Jour. Am. Chem. Soc., **37**, 1732 (1915).

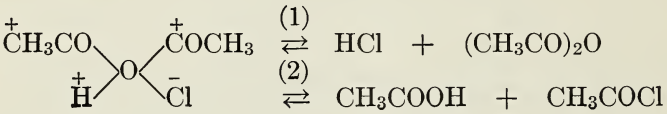
The hydrogen iodide first produces the oxonium salt, which may dissociate theoretically in three ways, but follows that course represented by equation 1, by reason of the excess of hydriodic acid used and the velocity of this reaction.

Application of the " onium " theory to the interaction of an alcohol and an acid may be shown as follows:



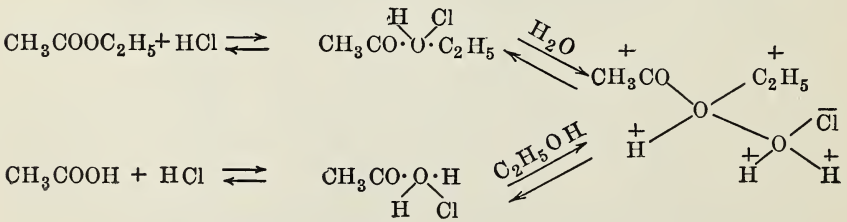
The addition of alcohol, or HX, or the removal of H_2O or RX causes the reaction to proceed according to equation 1.

The usual method for the preparation of acid anhydrides is interpreted according to the " onium " theory as follows:



In this case an excess of organic acid is used and the hydrochloric acid is removed by heat, thereby leading to conditions favorable for equilibrium and the production of acetic anhydride.

The action of hydrogen chloride as a catalytic agent, in both esterification and hydrolytic reactions, may be explained on the basis of " onium " compound formation. Until recently, the hydrogen $\overset{+}{H}$, and hydroxyl $\overset{-}{OH}$ ions of acids and bases have been assumed to be the active catalysts in such changes, but experimental evidence points to the importance of considering the catalytic effect of unionized molecules in these reactions. The application of the " onium " theory to the reaction possibilities of ethyl acetate, water, acetic acid and alcohol is expressed by the following equations:



According to Falk and Nelson,[1] this scheme accounts for the following facts:

1. The hydrogen chloride bears the same relation to the acid and the ester. It therefore catalyzes the reaction in both directions.
2. The onium compound formation depends on the strength of the acid catalyst. This is measured by the degree to which it breaks up in solution to form ions, a physical property similar to the chemical property of onium addition, which controls the rate of reaction with water or alcohol.
3. Increasing the concentration of water favors the production of acid; increasing the concentration of alcohol favors the production of ester.

On the basis of this primary formation of addition compounds, it is possible to formulate reactions such as sulphonation, nitration, aldol condensation, coupling, etc.

Classification of Organic Acids

Falk has suggested a classification[2] of organic acids which correlates the additive effect of the direct valences of the a-carbon atoms with the ionization constants of the acids, $(K \times 10^5)$, as calculated from Ostwald's dilution law, $K = \frac{y^2}{v(1-y)}$. The a-carbon atom is considered as exerting the greatest influence on the ionization constants of organic acids. An arbitrary classification may therefore be made on the basis of the direction of the valences, by which the a-carbon atom is combined with the atoms connected with it, the arrangement of the elements in the periodic system serving, in general, to indicate the electrical relations of the elements to each other in the production of a bond.

The four classes of acids which result from the above conception may be formulated as follows:

1

$\rightrightarrows$ C—COOH

Three electro-positive atoms connected with the a-carbon atom.

2

$\rightleftarrows$ C—COOH

[1] Loc. cit.

[2] Jour. Am. Chem. Soc., **33**, 1140 (1911).

Two electro-positive atoms and one electro-negative atom connected with the *a*-carbon atom.

3

$\rightleftarrows$C—COOH

One electro-positive atom and two electro-negative atoms connected with the *a*-carbon atom.

4

$\rightleftarrows$C—COOH

Three electro-negative atoms connected with the *a*-carbon atom.

Their ionization constants increase in the order 1, 2, 3, 4. Representative acids of the first group are acetic, caprylic, caproic, isobutyric, butyric, etc., whose ionization constants are less than .01. Class 2 includes acids like *a*-brompropionic, cyanacetic acid, etc., or those possessing ionization constants between .1 and .4, while Class 3 includes acids having ionization constants above 2, such as *a*-*a*-dibrompropionic acid, and dichloracetic acid. Group 4 comprises acids which are too highly ionized to give satisfactory dissociation constants, as for example, trichloracetic acid. Of the saturated dibasic acids, malonic acid is placed in Class 2, and succinic acid in Class 1. With regard to unsaturated acids, fumaric, on the basis of its ionization constant, is shown to be in Class 2 and acrylic in Class 1, while maleic acid,[1] depending upon the carboxyl group involved, functions either in accord with the acids of Class 1, or Class 3. The same principles have been applied to the acids of the benzene series, benzoic acid being a representative of Class 1, while salicylic acid is placed by Falk in Class 2.

A criticism of the above classification has been made by Fry. He concludes that, if the ionization constants of acids are dependent upon the direction of the valences of the *a*-carbon atom; all four and not three valences of the *a*-carbon atom should be taken into consideration.[1] That is to say, the valence of carboxyl, assumed as constant by Falk, may function either positively or negatively. Therefore, eight rather than four classes of organic acids are theoretically possible, and Fry represents them electronically as follows:

1. $\rightrightarrows$C$\rightarrow$COOH
2. $\rightleftarrows$C$\rightarrow$COOH
3. $\rightleftarrows$C$\rightarrow$COOH
4. $\rightleftarrows$C$\rightarrow$COOH
5. $\rightrightarrows$C$\leftarrow$COOH
6. $\rightleftarrows$C$\leftarrow$COOH
7. $\rightleftarrows$C$\leftarrow$COOH
8. $\rightleftarrows$C$\leftarrow$COOH

[1] Jour. Am. Chem. Soc., **34**, 664 (1912).

Fry has furnished evidence in support of the theory of the positivity and negativity of carboxyl, and has also shown that the properties [1] of acids are decidedly influenced by the polarity of this radical.

Nascent State and Nascent Action

Fry [2] advances the electronic conception of oxidation and reduction to explain the phenomena of nascent state and nascent action. The term nascent action connotes all those phenomena in which a substance at the moment of its liberation from compounds, performs reactions of which it is incapable in its ordinary condition.[3] In electronic terminology, oxidation corresponds to a loss, and reduction to a gain of negative electrons or charges by an atom. Ordinarily, hydrogen functions positively, and chlorine negatively. Each atom, however, may under special conditions function in the opposite polarity, negative hydrogen thereby becoming a reducing agent, losing negative electrons and reverting to positive hydrogen, and positive chlorine acquiring negative electrons, thus reverting to negative chlorine and becoming an oxidizing agent. The natural tendency of negative hydrogen and positive chlorine to revert to the positive and negative polarity, respectively, is illustrated below. The symbol $\ominus$ represents one unit of negative electricity and $\oplus$ one unit of positive electricity.

1. $\bar{H} \rightarrow \overset{+}{H} + 2\ominus$

2. $\overset{+}{Cl} \rightarrow \bar{Cl} + 2\oplus$

Nascent state has been defined by Fry as "an unstable condition of a substance, which manifests an adaptability and a tendency to lose or to gain electrons and thereby revert to a more stable condition." All reactions attributable to nascent action are apparently either oxidizing or reducing in their nature.

Application of the Electron Theory of Positive and Negative Valence to Some Reactions of the Aromatic Series

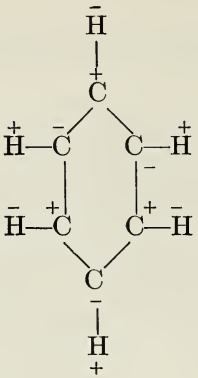
Application of the electronic conception of positive and negative valency to the atoms constituting the benzene molecule leads to the

[1] Loc. cit., Jour. Am. Chem. Soc., **36,** 257 (1914); Hanke and Koessler, Jour. Am. Chem. Soc. **40,** 1727 (1918.).

[2] Fry, Jour. Am. Chem. Soc., **36,** 270 (1914).

[3] Freund, Study of Chemical Composition, p. 327 (1904).

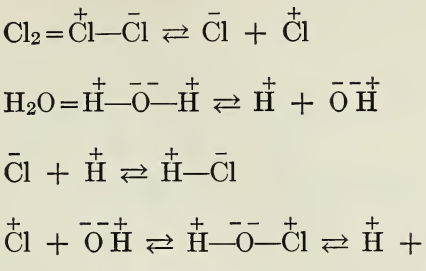
following formula for benzene [1] in which the hydrogen atoms in positions 1, 3, 5, function negatively, and those in positions 2, 4, 6, function positively.



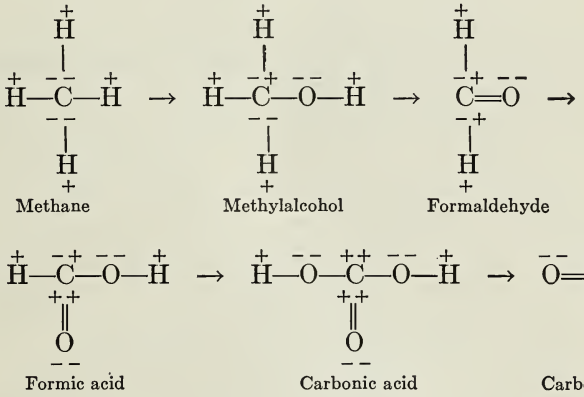
This formula presents a structural basis for the similarity in behavior of the *ortho*- and *para*-positions in contradistinction to the *meta*-position. The distinction between the 1, 3, 5, positions and the 2, 4, 6, is quite in accord with Collie's space formula. When a given substituent in the nucleus is positive, a hydrogen atom or substituent in the *meta*-position is of the same polarity. If the substituent is negative, the hydrogen atom or substituent in the *ortho*- or *para*-positions is positive. This formula therefore requires that the hydrogen atoms of the benzene ring function alternately as positive and negative, which is not illogical in the light of J. J. Thomson's statement that: " atoms of one and the same kind may become either positively or negatively electrified by the loss or gain of corpuscles," [2] and that " those with charges of opposite sign would combine to form a diatomic molecule." Therefore molecular hydrogen becomes $\overset{+}{H}—\overset{-}{H}$ and molecular chlorine $\overset{+}{Cl}—\overset{-}{Cl}$. Evidence of the existence of positive chlorine has been furnished by Noyes [3] and Stieglitz.[4] Noyes [5] has also presented evidence bearing on the positivity of iodine in diiodacetylene and, in general, the positivity of halogen in the $\equiv C \cdot Hal.$ linkages. The positivity of chlorine in hypochlorous acid may be shown in the

[1] Fry, Zeitschr. physikal. Chemie, **76**, 385 (1911); **76**, 398; **76**, 591.
[2] Electricity and Matter (Scribner's, 1907), p. 139.
[3] Jour. Am. Chem. Soc., **23**, 460 (1901); **35**, 767 (1913).
[4] Jour. Am. Chem. Soc., **23**, 797 (1901).
[5] Jour. Am. Chem. Soc., **42**, 991 (1920).

following transformations[1] illustrating the interaction of chlorine and water:



If the valence of an element is, n^2, it may function in $n+1$ different ways. For example, chlorine whose valency is 1, may function in two ways, and carbon with a valency of 4, in five ways, as is shown in the following scheme, representing the successive stages of the oxidation of methane, to carbon dioxide:

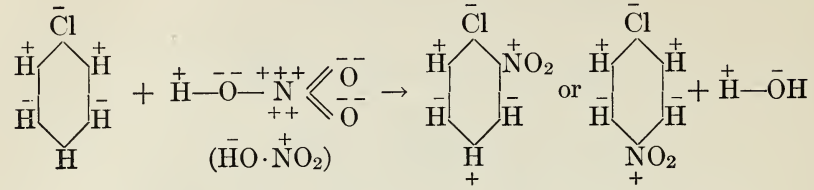


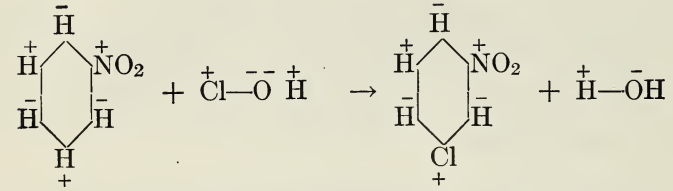
It is evident, therefore, that the direction of the valencies of the carbon atom in its compounds can not be determined[3] by the position of carbon in the periodic system, but, on the contrary, depends solely upon the polarity of the atoms (or radicals) which are connected with a given carbon atom.[4]

Examples of the application of the electronic formula of benzene and its derivatives will now be considered. Why is it that chlorobenzene undergoes nitration in the *ortho-* and *para*-positions whereas

[1] Fry, Zeitschr. physikal. Chemie, **76**, 388 (1911).
[2] Ibid.
[3] Fry, Jour. Am. Chem. Soc., **34**, 669 (1911).
[4] In contradistinction to Falk, loc. cit.

nitrobenzene is attacked by chlorine in the *meta*-position? The electronic equations [1] which follow are explanatory of this fact:

1. 

2. 

In equation 1, the electro-positive NO_2 group has replaced one of the two electro-positive hydrogen atoms (*ortho* or *para* positions). Since water-free chlorine will not act upon nitrobenzene. Fry considers that hypochlorous acid, with its positive chlorine, is the reagent which functions in reaction 2. If, therefore, halogen be positive it must replace a hydrogen atom *meta* to the positive NO_2 group. These facts reaffirm Fry's statement to the effect that when substituents are of the same sign or polarity they occupy positions which are *meta* to each other, whereas if two substituents are of opposite sign or polarity, they will occupy positions either *ortho* or *para* to each other.[2]

The positivity of the halogen in *m*-nitrochlorbenzene, as compared with the negativity of halogen in *p*-nitrochlorbenzene or *o*-nitrochlorbenzene, is likewise shown in the stability of the former and the reactivity of the two latter compounds with alkali.

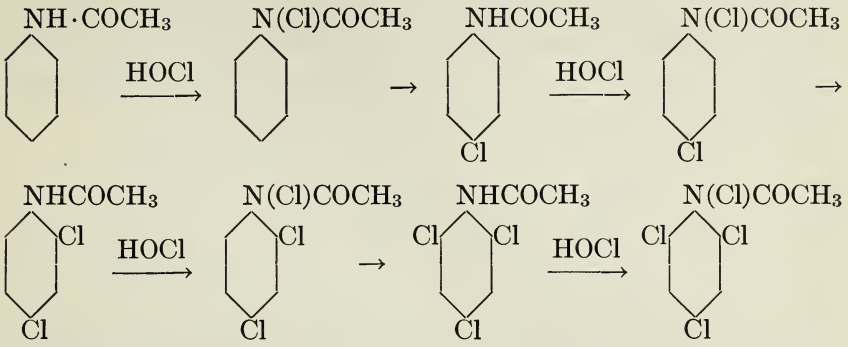
Evidence of the positivity of chlorine in positions 2, 4, 6, of the benzene nucleus is also shown in the characteristic rearrangements of the nitrogen substituted chloranilides.[3] For example, acetanilide when treated with hypochlorous acid gives phenylacetyl-nitrogen chloride, which is readily transformed into *p*-chloracetanilide. Successive treatments with hypochlorous acid, followed by rearrangement, will

[1] Fry, Zeitschr. physikal. Chemie, **76**, 384 (1911); Jour. Am. Chem. Soc., **36**, 248 (1914).

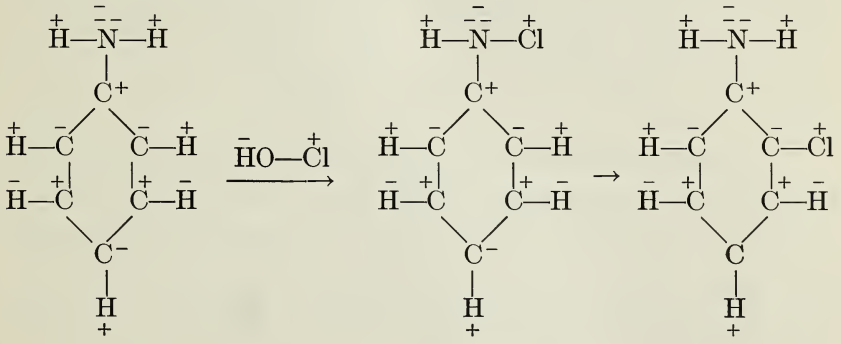
[2] Jour. Am. Chem. Soc., **36**, 248 (1914); **37**, 2368 (1915). See criticism by Brunel, Jour. Am. Chem. Soc., **37**, 709 (1915).

[3] Chattaway and Orton, Jour. Chem. Soc., **75**, 1046; Ber., **32**, 3572 (1899).

eventually give 2, 4, 6-trichlorphenylacetyl-nitrogen chloride, which is incapable of further rearrangement. These reactions are shown below:



Explanation of the positions occupied by the labile halogen atoms,[1] as well as the impossibility of introducing further halogen groups into the nucleus, is given in the fact that the amido group, NH_2, in aniline is negative, and must therefore occupy the position of a negative hydrogen atom in the benzene nucleus. If, therefore, positive chlorine from hypochlorous acid replaces one positive hydrogen atom of the amido group, this positive labile halogen atom, by reason of its polarity, can exchange positions with the positive hydrogen atoms (2, 4, 6) of the nucleus:



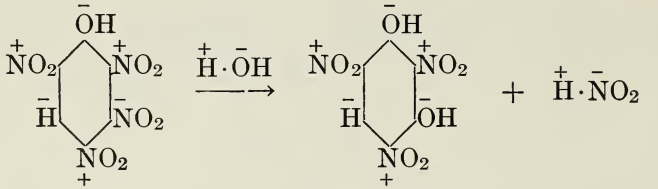
These facts further substantiate the positive equality of the 2, 4, 6, positions in the benzene nucleus and also, indirectly, the negativity of the 1, 3, 5, positions, on account of the inability of 2, 4, 6, trichlorphenylacetyl-nitrogen chloride to suffer rearrangement, through the replacement of another hydrogen of the nucleus with positive halogen.

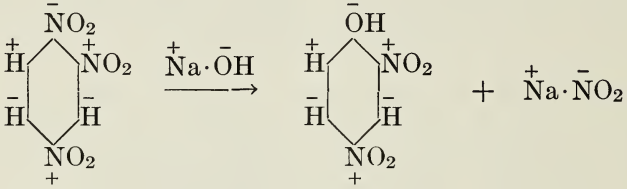
Proof of the alternate negativity and positivity [2] of the nucleus

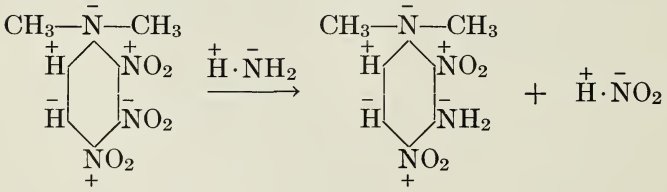
[1] Fry, Jour. Am. Chem. Soc., **34**, 667 (1912).

[2] Jour. Am. Chem. Soc., **38**, 1324 (1916).

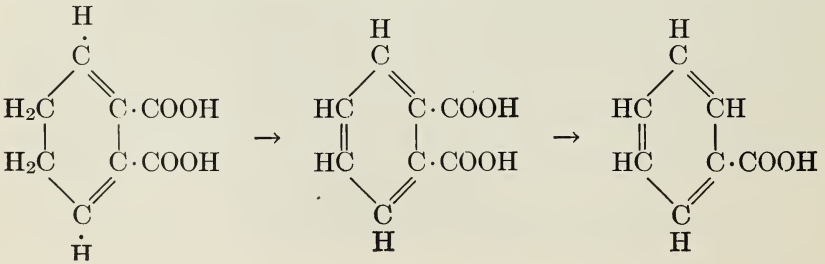
hydrogen atoms, or substituent groups, is also afforded in the case of hydrolysis of polynitro-compounds of the following types, in each of which, one of the nitro groups functions either positively or negatively. A negative nitro group is susceptible to the action of water alkalies, or ammonia, due to the replacement of the negative nitro group by negative hydroxy ($\bar{O}H$) or amino ($\bar{N}H_2$) radical:

1. 

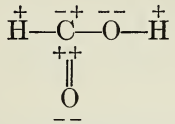
2. 

3. 

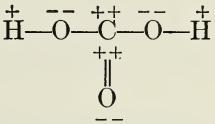
It has been stated above that eight classes of organic acids may theoretically be derived from a consideration of the directive valences of their *a*-carbon atoms. This assumption presupposes the possibility of positive as well as negative carboxyl groups. According to Fry, this receives corroboration in the oxidation of the $\Delta_{3,5,}{}^{-},{}^{-}\Delta_{2,4,}{}^{-}$, and $\Delta_{2,6,}{}^{-},{}^{-}$dihydrophthalic acids, where benzoic acid is formed in each case as the final product of reaction.



Since groups on adjacent carbon atoms must possess opposite polarities, it follows that one carboxyl group must be positive and the other negative. Referring to the electronic formulas of formic and carbonic acids, it will be observed that the carboxyl group in the former is negative, and in the latter positive.



Formic acid



Carbonic acid

In formic acid three of the valences of carbon are positive and the fourth negative, while in carbonic acid, all four valences are positive. Carbonic acid is therefore electronically capable of losing carbon dioxide, whereas formic acid is not. The characteristic oxidation reaction of the dihydrophthalic acids is therefore explained on the basis of the difference in polarity of the two carboxyl groups.[1] The above explanation is also applicable to the fact that *o*- and *p*-hydroxybenzoic acids are unstable, when heated with water or aniline, whereas *m*-hydroxybenzoic acid is stable under these conditions.[2] Fry has generalized this type of decomposition in the following words: "a carboxyl radical, either *ortho* or *para* to a negative hydroxyl, is positive, and therefore unstable, yielding carbon dioxide when heated with water or aniline. On the other hand, a carboxyl radical, *meta* to a negative hydroxyl radical, is negative, and therefore stable, not yielding carbon dioxide when heated with water or aniline." These conclusions are confirmed by the recent work of Hemmelmayr.[3]

The assumption that atoms or groups of atoms may function either positively or negatively, leads to the possibility of the existence of electronic isomers or "electromers."[4] For example, one can conceive of two forms of chlorobenzene, namely $\overset{+}{C_6H_5}\overset{-}{Cl}$ and $\overset{-}{C_6H_5}\overset{+}{Cl}$ or derivatives of $\overset{+}{C_6H_5}\overset{-}{H}$ and $\overset{-}{C_6H_5}\overset{+}{H}$ respectively. Although definite evidence has not yet been obtained concerning electromers of this halide, Fry concludes that the electromeric forms of benzene sulphonic acid, $C_6H_5SO_3H$, must be assumed to exist because hydrolysis

[1] Baeyer, Annalen der Chemie, 269, 178 (1892); Bruhl, Jour. prakt. Chemie (2), 49, 229 (1894); Cohen, Organic Chem. (1907) p. 461.

[2] Fry, Jour. Am. Chem. Soc., **36**, 257 (1914).

[3] Monatsh. Chemie, **34**, 365 (1913).

[4] Zeitschr. physikal. Chemie, **76**, 387 (1911).

of this compound in alkaline solution is productive of phenol and sulphurous acid, while in acid solution, or with superheated steam, the products of reaction are benzene and sulphuric acid.[1]

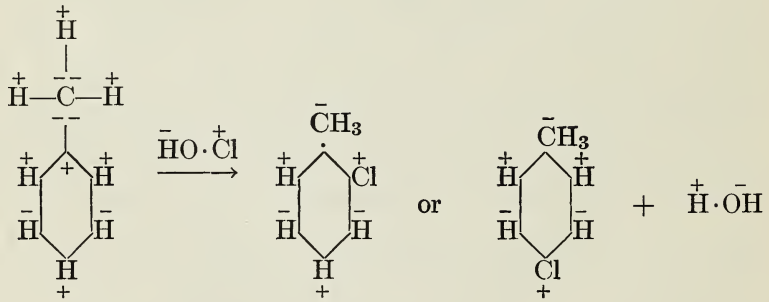
1. $C_6H_5{-}SO_3H + H{-}OH = C_6H_5{-}OH + H{-}SO_3H$
Alkaline hydrolysis

2. $C_6H_5{-}SO_3H + H{-}OH = C_6H_5{-}H + HO{-}SO_3H$
Acid hydrolysis

Fry has offered some interesting speculation on the mechanism of halogenation in the benzene nucleus and side chain.[2] The factors which are known to promote nucleus substitution are the following:

1. Presence of moisture.
2. Low temperatures.
3. Absence of sunlight.
4. Presence of halogen carriers.

These are the conditions which are peculiarly favorable for the formation of hypochlorous or hypobromous acids. Therefore, when toluene is halogenated under the above conditions, the presence of the electro-negative methyl group directs the positive chlorine of hypochlorous acid to the positive *ortho* or *para* positions,



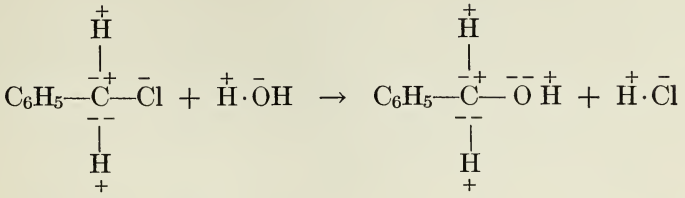
Furthermore, the fact that these nuclear positive halogens are firmly bound under conditions of hydrolysis is a proof of their polarity.

With regard to side-chain substitution, it is evident that the substituent halogen atom is negative, in that it is easily capable of

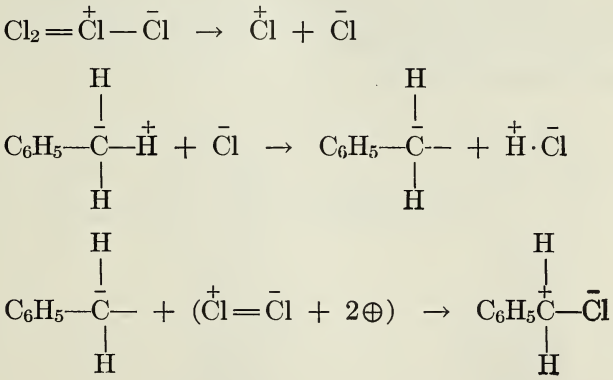
[1] Fry, Jour. Am. Chem. Soc., **36**, 265 (1914); Jones, Am. Chem. Jour., **48**, 26 (1912); Bray and Branch, Jour. Am. Chem. Soc., **35**, 1445 (1913).

[2] Jour. Am. Chem. Soc., **36**, 1035 (1914).

hydrolysis. For example, the hydrolysis of benzyl chloride is represented by the following electronic equation:



Moreover, the reaction is reversible in the presence of an excess of hydrochloric acid. The mechanism of side-chain substitution is apparently more complex than that of nuclear. This reaction is facilitated by heat, light, and the absence of water. The substituting agent, molecular halogen, dissociates into positive and negative halogen atoms, of which the latter combines with a positive hydrogen atom of the methyl group, forming hydrogen chloride, $\overset{+}{H}\overset{-}{Cl}$. This necessitates the conclusion that the remaining positive halogen atom acts as an oxidizing agent, converting the negative valence of carbon to a positive valence, and being itself reduced to negative chlorine. These changes may be represented as follows:

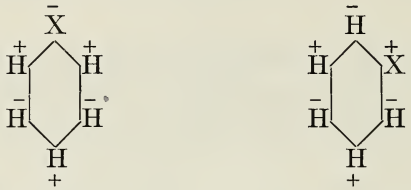


Heat and the photochemical action of light effect the conversion of positive to negative halogen.

The electronic formula of benzene presents an explanation of the Brown and Gibson rule,[1] which is stated by these investigators as follows: " when X is naturally to be regarded as a derivative of HX, then C_6H_5X gives *ortho* and *para* di-derivatives; and when X is

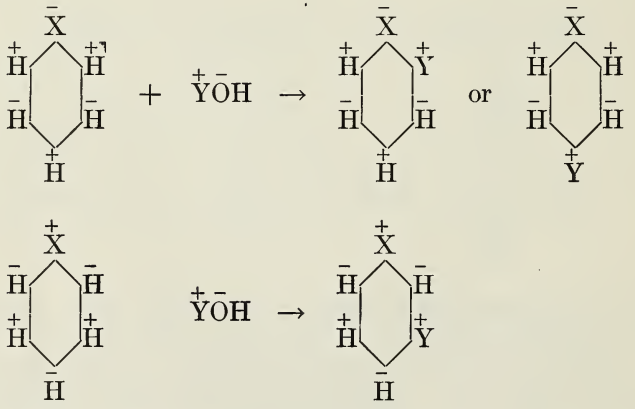
[1] Jour. Chem. Soc., **61**, 366 (1892).

naturally to be regarded as a derivative of HOX, then C_6H_5X gives *meta* di-derivatives." As previously shown, X in compounds such as HX functions negatively, and X in compounds like HO X, positively, as for example, Cl in HOCl. Therefore a substituent X, which is a natural derivative of H O X, or C_6H_5X, occupies the position of a positive hydrogen atom in the benzene nucleus, while a substituent X which is a natural derivative of H X, or C_6H_5X, occupies the position of a negative hydrogen atom, i.e.,



In nuclear substitution it may be assumed that the entering substituent is positive, this being evidenced by the fact that either H OH, or some binary compound of the formula H B is always eliminated during this type of reaction. It is evident, therefore, that X must govern the *meta* position and X, the *ortho* and *para* positions in accord with the previously stated electronic rule for benzene substitution. It should be emphasized that the entrance of Y as a positive substituent does not preclude its reversion to the radical of opposite polarity.

The following equations will serve to illustrate the action of Y OH on both C_6H_5X and C_6H_5X:

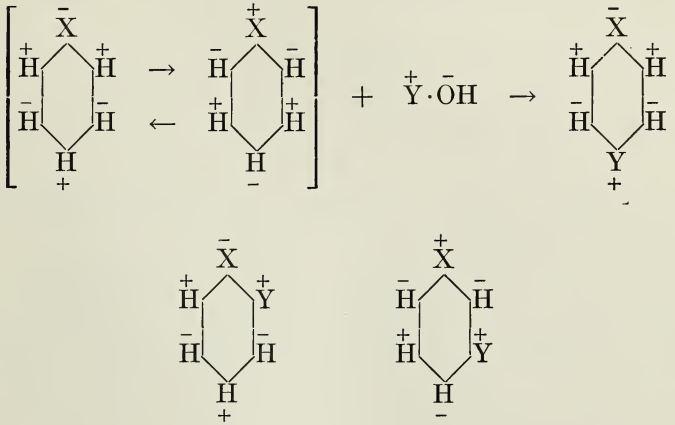


A mixture of *ortho*, *para* and *meta* derivatives is often produced in a given reaction.[1] This has been explained on the basis of elec-

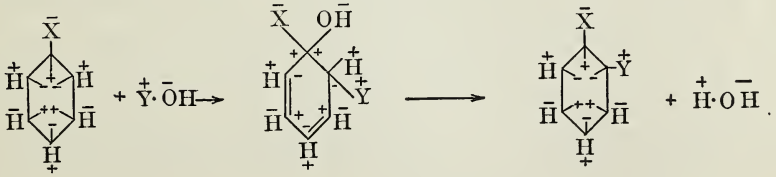
[1] Fry, Jour. Am. Chem. Soc., **37**, 864 (1915).

tronic tautomerism, which is shown in the following equations by the partial transformation of a negative substituent X into an atom of opposite polarity. In this case, the introduction of a second substituent would produce a preponderance of *ortho* and *para* derivatives, together with a small amount of the *meta* di-derivative.

$$\overset{+}{C_6H_5}\overset{-}{X} \rightleftarrows \overset{-}{C_6H_5}\overset{+}{X}$$



The interpretation of the hypothesis of Holleman [1] regarding benzene substitution from the electronic standpoint [2] is illustrated by the following formulas showing the action of a reagent $\overset{-}{OH}\cdot\overset{+}{Y}$ on a derivative $\overset{+}{C_6H_5}\cdot\overset{-}{X}$, whereby an addition product is first formed. The elimination of $\overset{+}{H}\cdot\overset{-}{OH}$ from the latter produces the final product. *Meta* and *para* substitution can be similarly shown.



This electronic formulation of substitution has met with criticism from Holleman.[3]

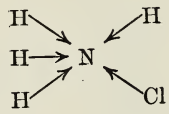
[1] Rec. trav. chim. des Pays-Bas, **33**, 1 (1914).

[2] Holleman, Jour. Am. Chem. Soc., **36**, 2495 (1914); cf., Fry, Jour. Am. Chem. Soc., **37**, 883 (1915).

[3] Loc. cit.

Valence Number

In applying the electronic theory to explain the phenomenon of valence, two outstanding ideas are embodied in the term valence number of an atom. Bray and Branch [1] have suggested that this be differentiated by the terms *polar number* and *total valence number.* For example, in ammonium chloride,



the total valence number of nitrogen is 5, while the polar number, representing the algebraic sum of the valences, is −3. The valence of nitrogen in ammonium chloride is therefore represented as (−3, 5), the polar number being written first. Similarly the valence of carbon in methane would be (−4, 4) and in carbon tetrachloride (+4, 4).

Bray and Branch express doubt, however, regarding the application of this electronic conception of valence number, in all cases, citing in particular the saturated hydrocarbons, concerning which there is frequently a question as to the actual polar valency of the individual carbon atoms. Moreover, methane and carbon tetrachloride do not offer the striking contrast in properties which might be expected from their respective polar valences (−4, 4) and (+4, 4). This is in decided contrast to the analogous case of ammonia (−3, 3) and nitrogen trichloride (+3, 3). In view of these facts, they favor using the ordinary organic structural formulas and altering them only where there are definite evidences of polar unions. This theory permits of the appearance of both polar and non-polar bonds in the same molecule, the former being one in which an electron has passed from one atom to another and the latter, one in which there is no movement of electrons.[2] A polar bond is represented by the arrow → (Falk), or by polarity symbols, + − (Fry); for example, $H \rightarrow Cl$, or $\overset{+}{H}—\overset{-}{Cl}$.

[1] Jour. Am. Chem. Soc., **35**, 1440 (1913).

[2] Attention should be called here to Langmuir's " octet " theory of valency which has been applied to the structure of inorganic compounds and certain organic nitrogen compounds, and which gives an interesting theoretical explanation of their formation. For complete information see the following publications: G. N. Lewis, Jour. Am. Chem. Soc., **38**, 762 (1916); Langmuir, Jour. Am. Chem. Soc., 41, 868 (1919); ibid., **41**, 1543; Proc. Nat. Acad. Sci., **5**, 252 (1919); Jour. Ind. Eng. Chem., **12**, 385 (1920); Jour. Am. Chem. Soc., **42**, 274 (1920).

Two groups of compounds can be made on the basis of the above assumptions. The first group comprises those compounds whose valence bonds are chiefly polar, and the second group, those whose valence bonds are mainly non-polar. The first class is characterized by high dielectric constants, the property of forming ions, and in general by high chemical activity. The opposite properties are possessed by the second class. In other words, the first class corresponds to the inorganic class of compounds and the second to that of the organic compounds.

In a commentary on the speculations of Bray and Branch, G. N. Lewis,[1] has further developed the conception of polar and non-polar compounds, and has contributed the following scheme, which may serve to show the salient differences between the polar and non-polar types of compounds:

Polar	*Non-Polar*
Mobile	Immobile
Reactive	Inert
Condensed structure	Frame structure
Tautomerism	Isomerism
Electrophiles	Non-electrophiles
Ionized	Non-ionized
Ionizing solvents	Non-ionizing solvents
High dielectric constants	Low dielectric constants
Molecular complexes	No molecular complexes
Association	No association
Abnormal liquids	Normal liquids

It should be pointed out that the differentiation as to polar or non-polar compounds is not necessarily a sharply defined one, for, as Lewis states,[2] "it must not be assumed that any one compound corresponds wholly and at all times to either one type."

Falk and Nelson [3] do not consider the non-polar valence view as a sufficiently broad basis upon which to classify valence phenomena in organic chemistry. In the following series of transformations they point out that the non-polar view would represent the replacement of

$$CH_4 \rightarrow CH_3OH \rightarrow CH_2O \rightarrow CH_2O_2 \rightarrow CO_2$$

[1] Jour. Am. Chem. Soc., **35**, 1448 (1913); **38**, 762 (1916).
[2] Loc. cit.
[3] Jour. Am. Chem. Soc., **36**, 210 (1914).

hydrogen by oxygen or hydroxyl, with no change in the electrical charge on the carbon atom, taking no cognizance of the fact that oxidation is involved, and that this reaction is generally interpreted on an electronic basis. Furthermore, the chlorination of methane would consist in the mere replacement of hydrogen by chlorine.

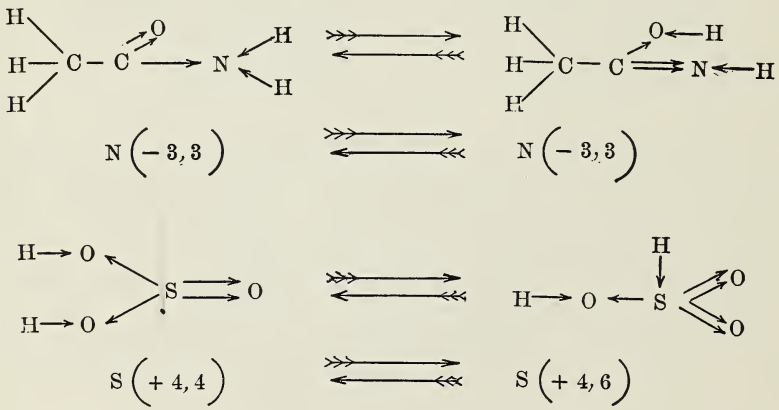
A classification of tautomeric changes made on the basis of the new conception of *polar number* and *total valence number* [1] leads to two groups of reactions, namely:

1. Tautomeric changes in which no change in polar number is involved.

   (*a*) No change in total valence number.
   (*b*) Change in total valence number.

2. Tautomeric changes in which the polar numbers of two elements are altered.

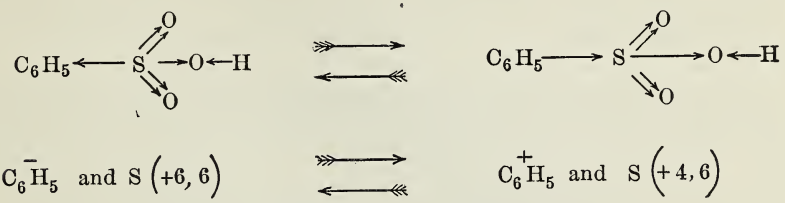
Reactions characteristic of Class 1, are those represented by the well-known examples of α, β or (1, 2), and α, γ or (1, 3) tautomerism, which involve a shifting of a hydrogen atom from one part of the molecule to another. An illustration of α, β-tautomerism (Class 1*b*), is that of sulphurous acid, while an example of α, γ-isomerism (Class 1*a*), is shown in the tautomerism of acetamide. These equilibria are expressed as follows:



Benzene sulphonic acid, $C_6H_5SO_3H$, is an excellent example of Class 2, which includes tautomeric changes involving a change of

[1] Bray and Branch, Jour. Am. Chem. Soc., **35**, 1444 (1913).

polar number of two constituent elements. This tautomerism of benzene sulphonic acid is manifested in its difference in behavior on hydrolysis in acid and alkaline solution, the former producing benzene and sulphuric acid, the latter, phenol and sulphurous acid.



The Beckmann Rearrangement

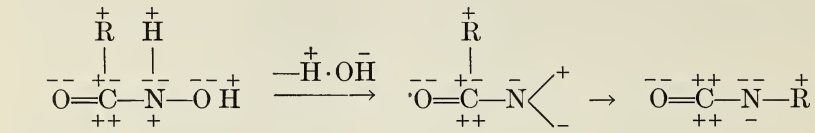
Reference will be made to the Beckmann rearrangement in the chapter on Molecular Rearrangements where the various theories which have been proposed to explain the mechanism of this change have been discussed. According to Stieglitz, the molecular rearrangements of halogenated acid amides RCONH. Hal., hydroxamic acids RCONHOH, dihydroxamic acids RCONHOCOR, acid azides and ketoximes are all induced by the presence of univalent nitrogen, which results from a dissociation of the molecule undergoing change, whereby the valence of nitrogen is reduced from 3 to 1. The predisposing cause of rearrangement is, therefore, the free valency of univalent nitrogen. His conclusions are summarized in a paper published by Stieglitz and Stagner.[1]

Jones[2] correlates Stieglitz' theory with the electronic hypothesis, and calls attention to the fact that in all the reactions, classified under the Beckmann rearrangement, the transformation is accompanied by a process of intramolecular oxidation and reduction. That is to say, there is a tendency of the system to revert to one in which, electronically speaking, the carbon atom is as fully oxidized as possible and the nitrogen atom as fully reduced as possible. In other words, where Stieglitz attributes the rearrangement to the potency of the free valencies of univalent nitrogen, according to this electronic conception the change is dependent on the potency of a carbon atom to lose negative electrons and of the nitrogen atom to acquire them.

[1] Jour. Am. Chem. Soc., **38**, 2064 (1916).

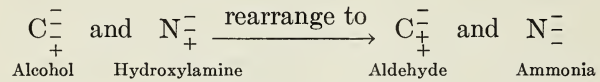
[2] Am. Chem. Jour. **50**, 440 (1913); Jones and Sneed, Jour. Am. Chem. Soc., **39**, 674 (1917).

The rearrangement of a hydroxamic acid is expressed electronically as follows:

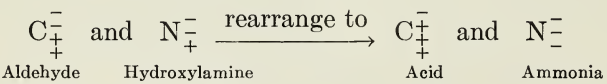


This view of the Beckmann transformation leads to a classification of this type of reaction into groups determined by the state of oxidation which the carbon atom shows prior and subsequent to rearrangement. In all of these rearrangements the nitrogen atom is considered to be in a state of oxidation corresponding to that of nitrogen in hydroxylamine.

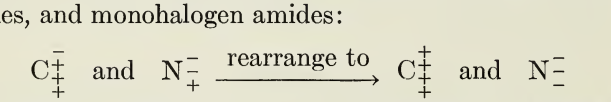
Group 1. Azides, monosubstituted hydroxylamines, such as triphenylmethylhydroxylamine, and mono-bromoamines such as triphenylamine bromide:



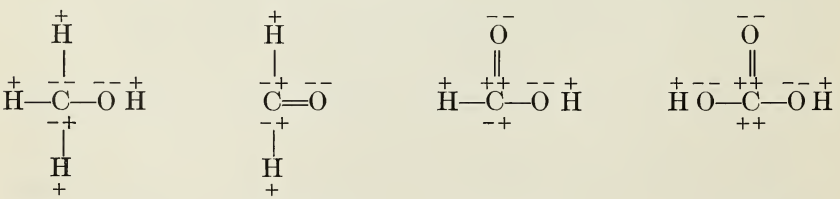
Group 2. Aldoximes and ketoximes:



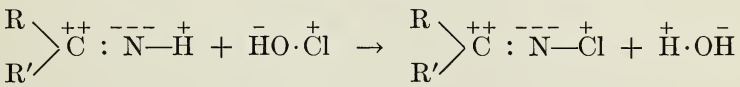
Group 3. Hydroxamic acids, their salts and esters, amidoximes, acid azides, and monohalogen amides:



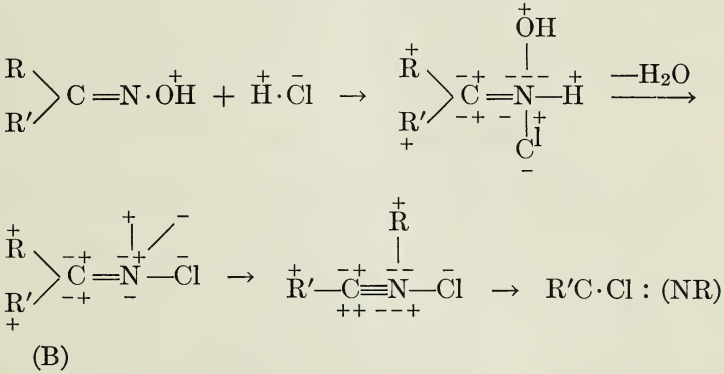
The statement under each symbol—alcohol, hydroxylamine, etc., indicates the state of oxidation as compared with that of the atom in compounds where its polarity is similar. With regard to carbon, the stages of oxidation referred to are expressed electronically as follows:



At this point mention should be made of the fact that Stieglitz,[1] in support of his theory, was unable to bring about rearrangement of stereoisomeric chlorimides, RR'C=NCl, thereby showing that these compounds are not intermediate products of a Beckmann rearrangement of oximes. According to their electronic constitution, these chlorides of Stieglitz' should be capable of undergoing rearrangements on account of the positive polarity of the halogen atom. That the halogen in such compounds is positive is apparent from consideration of the electronic equation showing their formation from imidoketones and hypochlorous acids. More recent investigations have led Stieglitz[2] to con-



sider a third electromer of the chlorimidoketone, an assumption which is of broad significance concerning the mechanism of the Beckmann rearrangement, and which is an extension of his original theory. The mechanism of rearrangement of an oxime by the action of hydrochloric acid may be expressed electronically as follows:[3]



(B)

According to this interpretation, the hydroxyl group in the oxime is considered to be positive.[4] Its tendency, therefore, is to change to a stable negative condition, the nitrogen atom furnishing the two requisite electrons to the oxygen atom. Water is then eliminated with the production of the chloride B. According to Stieglitz, this product is an ammonium salt with two of the nitrogen valencies unsaturated

[1] Ber., **43**, 782 (1910).

[2] Jour. Am. Chem. Soc., **36**, 288 (1914.)

[3] See criticism by A. Michael, Jour. Am. Chem. Soc., 42, 787, 1232 (1920).

[4] The views of Jones and Stieglitz are not at variance. Jour. Am. Chem. Soc., **36**, 288 (1914).

in the same way as they are unsaturated in univalent nitrogen derivatives. It is these unsaturated valencies which are considered to be the direct cause of the rearrangement, two electrons passing from the carbon atom to the nitrogen to give this a normal and stable charge such as it has in ammonium salts. With the change of electronic forces, the positive radical R, nearest to the field of force, is lost by the now positive carbon and carried to the now negative nitrogen. Such a series of changes accounts for the nature and action of the reagents used to accomplish the rearrangement (acid dehydrating agents), and it gives a rational picture of the electrical forces in play in the rearrangement of the valencies of the molecule. Such a course would also account for the influence of stereoisomerism on the rearrangement,[1] if such an influence should finally be established as beyond doubt—the radical (R in the above illustration) nearest to the electrical fields of force, produced by the migration of electrons from carbon to nitrogen, passing under the influence of this force to the nitrogen. According to this view the rearranging product B would be a third electromer of of the chlorimido ketones of Stieglitz and Peterson [2] and would represent a logically active form of the chloride which Hantzsch assumed as the intermediate product in the rearrangement of ketoximes by the action of hydrochloric acid. This fundamental difference between the latter's theory and the one now developed should be carefully noted.

Hydrogen and Hydrocarbo Bases

Franklin,[3] Kraus and others have developed a new system of acids, bases and salts, the derivaties of which have been termed " ammono," in contradistinction to the " aquo " or ordinary oxygen acids or bases. For example, the neutralization phenomena in both types may be contrasted as follows:

$$\underset{\text{Aquo acid}}{CH_3COOH} + \underset{\text{Aquo base}}{KOH} = \underset{\text{Aquo salt}}{CH_3COOK} + H_2O$$

$$\underset{\text{Ammono acid}}{CH_3CONH_2} + \underset{\text{Ammono base}}{KNH_2} = \underset{\text{Ammono salt}}{CH_3CONHK} + NH_3$$

On the basis of comparison, Jones[4] has suggested that certain metallic hydrides, NaH, etc., and metallic alkyls, such as zinc alkyls, be termed " hydrogen bases " and " hydrocarbo bases " respectively. The reactions of either type show a similarity to those of the ammono

[1] Schroeter, Ber., **44** (1911).
[2] Loc. cit.
[3] Am. Chem. Jour., **45**, 291 (1912).
[4] Jour. Am. Chem. Soc., **40**, 1259 (1918).

and aquo derivatives. For example, the negative alkyl group of the metallic alkyls (hydrocarbo bases) enters into a large number of reactions involving the displacement of the same with other negative groups. This is also true to a more limited extent with regard to the hydrogen bases. A few examples will serve to show their chemical behavior:

$$NaH + HX = NaX + \overset{+}{H}\cdot\overset{-}{H}$$

$$Zn(CH_3)_2 + 2HCl = ZnCl_2 + 2\overset{+}{H}\cdot\overset{-}{C}H_3$$

$$ZnR_2 + 2HOH = Zn(OH)_2 + 2\overset{-}{R}\cdot\overset{+}{H}$$

$$ZnR_2 + 2NH_3 = Zn(NH_2)_2 + 2\overset{-}{R}\overset{+}{H}$$

Of interest from an electronic standpoint is the fact that both the hydrogen bases and the hydrocarbo bases are reducing agents, a property sharply distinguishing them from the ammono and aquo bases. This property is due to the tendency of negative hydrogen and negative alkyl to lose negative electrons, and assume positive charges, i.e.,

$$\overset{-}{H} \xrightarrow{\text{—elec.}} H \xrightarrow{\text{—elec.}} \overset{+}{H}$$

$$\overset{-}{C}H_3 \xrightarrow{\text{—elec.}} CH_3 \xrightarrow{\text{—elec.}} \overset{+}{C}H_3$$

The interaction of carbon dioxide and sodium hydride is an excellent example of this property.

$$\overset{--}{O}=\overset{++}{C}=\overset{--}{O} + \overset{+}{Na}\cdot\overset{-}{H} = \overset{--}{O}=\overset{++}{C}(\overset{++}{H})-\overset{--}{O}-\overset{+}{Na} \rightarrow O=\overset{++}{C}(\overset{+-}{H})-\overset{--}{O}-\overset{+}{Na}$$

Moreover the well-known synthetic reactions, utilizing the zinc alkyls, or Grignard reagents, probably involve, apart from the usual additive reactions, processes of reduction, effected by the negative alkyl radicals of the metallic organic compounds. Thus, in the following reactions, the carbon atom is reduced from $\overset{-+}{C}$ to $\overset{--}{C}$ by the change of $\overset{-}{C}H_3$ to $\overset{+}{C}H_3$:

$$\overset{+}{H}_2\overset{+-}{C}=\overset{--}{O} + \overset{+}{Mg}(\overset{-}{C}H_3)(\overset{-}{Br}) = \overset{+}{H}_2\overset{-+}{C}(\overset{-}{C}H_3)(\overset{--}{O}\,\overset{++}{Mg}\,\overset{-}{Br}) \xrightarrow{H_2O}$$

$$\overset{+}{H}_2\overset{-+}{C}(\overset{+}{C}H_3)(\overset{--}{O}-\overset{+}{H}) + MgBr\cdot OH$$

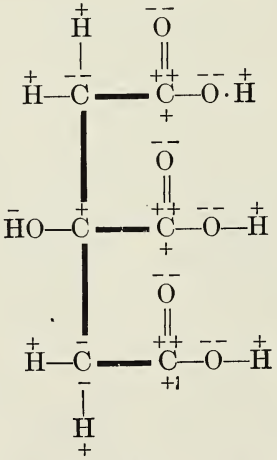
The mercury and lead alkyls afford an interesting and very apparent proof of electromeric possibilities, in the fact that the former are hydrolyzed by acetic acid, giving one molecule of hydrocarbon and one molecule of alcohol, while the latter give three molecules of hydrocarbon and one molecule of alcohol. In the first case, one alkyl group functions positively and the other negatively, while in the tetra-alkyl lead complex, one alkyl functions positively and three negatively. These facts may be expressed as follows:

1. $$\overset{-+}{\mathrm{Hg}}\begin{matrix}\diagup\overset{-}{\mathrm{R}}\\ \diagdown\overset{+}{\mathrm{R}}\end{matrix} + \overset{+}{\mathrm{H}}\cdot\overset{-}{\mathrm{OH}} = \mathrm{Hg} + \overset{+}{\mathrm{R}}\cdot\overset{-}{\mathrm{OH}} + \overset{-}{\mathrm{R}}\cdot\overset{+}{\mathrm{H}}$$

2. $$\begin{matrix}\overset{-}{\mathrm{R}}\\ \overset{-}{\mathrm{R}}\end{matrix}\!\!>\overset{++}{\underset{+-}{\mathrm{Pb}}}\!\!<\begin{matrix}\overset{-}{\mathrm{R}}\\ \underset{+}{\mathrm{R}}\end{matrix} + \overset{+}{\mathrm{H}}\cdot\overset{-}{\mathrm{OH}} + 2\mathrm{CH_3COOH}$$
$$= 3\overset{-}{\mathrm{R}}\overset{+}{\mathrm{H}} + \overset{+}{\mathrm{R}}\overset{-}{\mathrm{OH}} + \mathrm{Pb(C_2H_3O_2)_2}$$

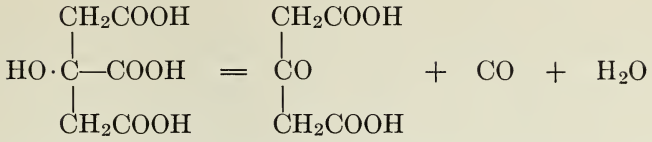
The Electronic Constitution of Certain Acids

It has been shown by Fry that the carboxyl group may function either positively or negatively. A further confirmation of this possibility has been given in the deductions concerning the electronic constitutions of acetoacetic and citric acids, and some of their derivatives.[1] The electronic formula of citric acid may be represented as follows, the position of bonds of undetermined polarity being shown by the heavy black lines:

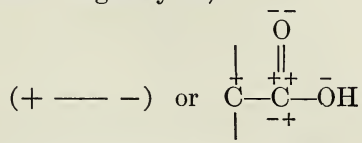


When citric acid is treated with fuming sulphuric acid at 60°–70° the *central* carboxyl group is eliminated as carbon monoxide. with formation of acetone dicarboxylic acid:

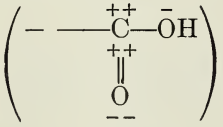
[1] Hanke and Koessler, Jour. Am. Chem. Soc., **40**, 1727 (1918).



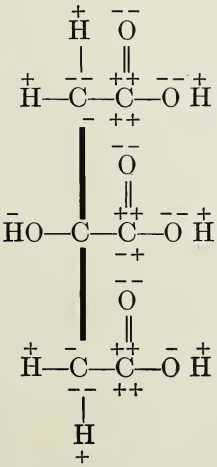
This reaction speaks for a difference in polarity between this radical and the two extreme carboxyl groups. The formula of active carbon monoxide is $\overset{-+}{C}\overset{--}{=}\overset{++}{O}$; therefore the bond uniting the middle carboxyl group in citric acid would logically be,



while the two extreme carboxyl groups must be,

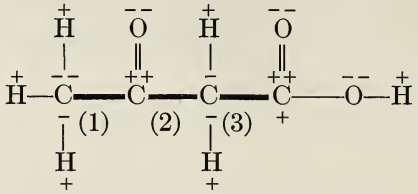


This latter view is supported by the fact that the two carboxyl groups of acetone dicarboxylic acid may be eliminated as CO_2 and not as CO by heating with mineral acids or alkalis. In other words, only carboxyl groups containing carbon in its highest state of oxidation, $\overset{++}{C}$, are electronically capable[1] of losing CO_2 in chemical reactions. The formula of citric acid may now be written as follows:

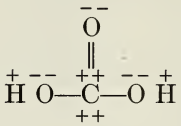


[1] Fry, Jour. Am. Chem. Soc., **34**, 664 (1913); **36**, 256 (1915).

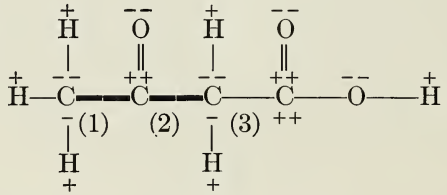
The fact that acetone dicarboxylic acid can be transformed into acetone makes it evident that if the electronic formula of the latter could be established, the polarity of the doubtful bonds in the former, and also citric acid, would thereby be determined. Turning to acetoacetic acid, the following formula presents an electronic view of its structure:



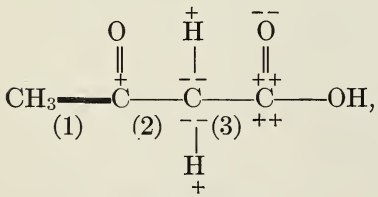
By " ketonic " hydrolysis the carboxyl group may be eliminated as carbonic acid



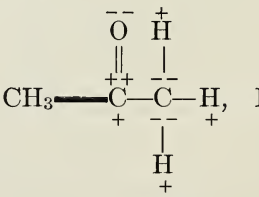
or CO_2 and acetone formed. Bond 3 must therefore be (− +) and the formula of acetoacetic acid may be electronically expressed as follows:



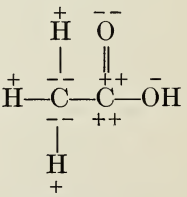
Acid hydrolysis of acetoacetic acid is productive of two molecules of acetic acid, the hydrogen atom of $\overset{+}{H}\cdot\overset{-}{O}H$ going to the α-carbon atom of the acid. Bond 2 may therefore be written (+ −), and the structures of acetoacetic acid, acetone and acetic acid become respectively:



Acetoacetic acid



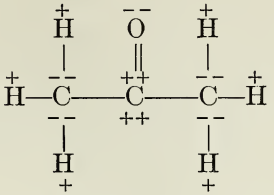
Acetone



Acetic acid

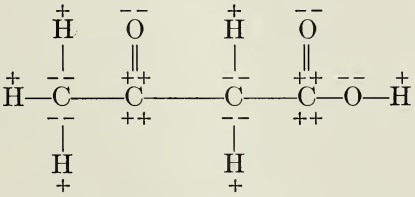
Since, however, two molecules of acetic acid result from the acidic hydrolysis of acetoacetic acid, it follows that the electronic formula

of acetone should be the symmetrically constituted,

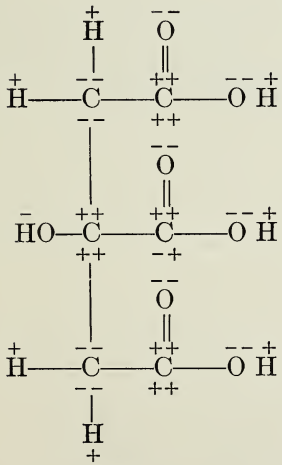


The formula of acetic acid receives futher confirmation in the light of its formation from ketene, $CH_2{=}CO$ and water, $\overset{+}{H}\ \overset{-}{OH}$.

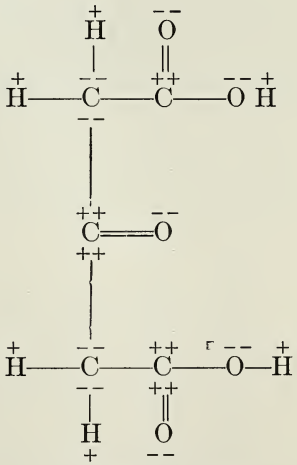
The formula of acetone now being established, the polarity of the doubtful bonds in acetoacetic, acetone dicarboxylic acid, and citric acid becomes apparent. Their electronic fo mulas may now be represented as follows:



Acetoacetic acid



Citric acid



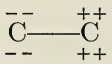
Acetone dicarboxylic acid

The Electronic Constitution of Normal Carbon Chain Compounds

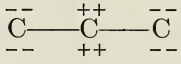
It is difficult to assign definite electronic formulas to acyclic or chain hydrocarbons. The difficulty arises in the fact that the proper dis-

tribution of polarity on the adjacent carbon atoms cannot be made. Cuy [1] has recently called attention to the fact that the electronic formulas of acetoacetic, citric, acetone dicarboxylic and acetic acids, derived by Hanke and Koessler,[2] show a striking regularity with regard to the alternate positivity and negativity of the carbon atoms. Considering only the carbon atoms and their polarity, the simplified formulas of these acids may be given as follows:

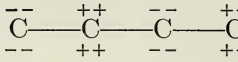
Acetic acid,



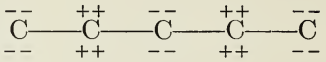
Acetone,



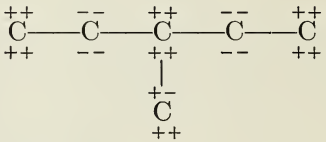
Acetoacetic acid,



Acetone dicarboxylic acid,



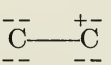
Citric acid,



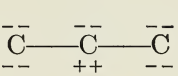
It is assumed by Cuy that carbon atoms in a chain have a natural tendency to appear alternately positive and negative, whenever possible. For example, the positive and negative charges in an homologous series of the paraffines are presumably distributed as follows:

1.

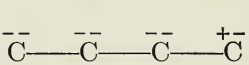
2.



3.



4.



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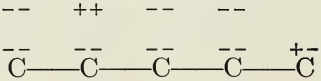

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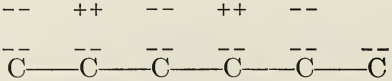
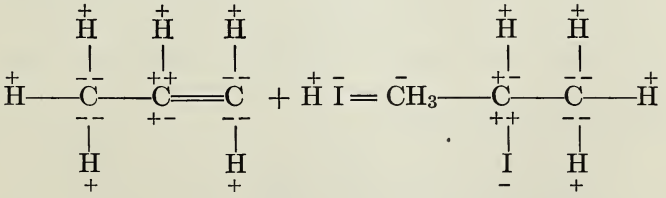


[1] Jour. Am. Chem. Soc., **42**, 503 (1920).
[2] Jour. Am. Chem. Soc., **40**, 1726 (1918).

The compounds containing an even number of carbon atoms form an homologous series and those containing an odd number of carbon atoms form another homologous series, since Class 1 differs from Class 3 by $\overset{+-}{C}\!-\!\!-\!\overset{+-}{C}$, and Class 3 differs from Class 5 by the same $\overset{+-}{C}\!-\!\!-\!\overset{--}{C}$ group. Similarly Class 2 differs from Class 4, and Class 4 from Class 6 by $\overset{--}{C}\!-\!\!-\!\overset{--}{C}$. But 1 differs from 2 by a $\overset{+-}{\underset{-}{C}}$ group, and 2 from 3 by $\left[\overset{++}{C}\!-\!\!-\!\overset{--}{C}\right] - \left[\overset{+-}{C}\right]$. Similar formulas may be written and compared in the case of other homologous series with the same result. In other words, the members containing an even number of carbon atoms and those containing an odd number give two distinct homologous series from an electronic view point.

This tendency to assume alternately positive and negative charges is reflected in the various physical properties of the compounds, such as melting points and boiling points. Moreover, this hypothesis admits of interesting and logical explanations of various addition-reactions of hydrogen halides to unsaturated hydrocarbons. For example, Markownikoff's rule states: "when unsymmetrically constructed hydrocarbons of the series $C_n H_{2n}$ combine with hydrogen iodide, the iodine is added to the least hydrogenated carbon atom." The addition of hydrogen iodide to propylene, which follows Markownikoff's rule, is also in accord with the above described theory of alternating polarity. The least hydrogenated carbon atom of propylene would be electropositive in comparison with the extreme carbon atom. Therefore, the positive hydrogen of hydrogen iodide adds to the latter, by reason of the free negative valence of this atom, while negative iodine becomes attached to the intermediate carbon atom, through the medium of the free positive valency of the latter. These facts are expressed in the following electronic equation:



Kinetic Hypotheses Accounting for Chemical Combination

The reactions which have hitherto been formulated on the basis of the electronic conception have been largely viewed from the standpoint of the theory that chemical combination involves the transfer

of valence electrons from one atom to another, on the basis of the original suggestion of J. J. Thomson. Ramsay,[1] however, has discussed the possibility of the electron taking a position between any two atoms held in combination, and has developed this conception,[2] showing through models the magnetic effects which would serve to bring about combination between two given atoms, by reason of the rotation of electrons in adjoining parts of the atoms. Bohr [3] has also considered the possibility of atomic combination through the result of electrons rotating about a path joining the positive nuclei of two atoms. An exposition of this "magneton" conception of atomic structure has been given by Parsons.[4] Interesting electronic theories in explanation of isomerism have been suggested by Garner,[5] on the basis of Bohr's hypothesis and by Allen [6] on the basis of Parson's magneton theory.

Recently W. A. Noyes has offered a kinetic hypothesis explanatory of the function of electrons in producing chemical combination between atoms. He writes as follows:[7] "let us suppose that two atoms which have an affinity for each other are brought close together. A valence electron which is rotating around a positive nucleus in the first atom may find a positive nucleus in the second atom sufficiently close, so that it will include the latter in its orbit, and it may then continue to describe an orbit about the positive nuclei of the two atoms. During that portion of the orbit within the second atom, that atom would become, on the whole, negative while the first atom would be positive. During the other part of the orbit, each atom would be electrically neutral, and the atoms might fall apart. When we remember, however, the tremendous velocity of the electrons, and the relatively sluggish motions of the atoms, it seems evident that the motion of an electron in such an orbit might hold two atoms together. In ionization the electron would, of course, revolve about the nucleus of the negative atom leaving the other atom positive. It seems impossible to explain ionization otherwise than on the supposition of the complete transfer of the electron. This complete transfer in ionization is one of the strongest arguments against the magneton theory as the only explanation of chemical combination."

[1] Jour. Chem. Soc., 93, 774 (1908).
[2] Proc. Roy. Soc., (A) 92, 451 (1916).
[3] Phil. Mag., **26**, 1, 476, 857 (1913).
[4] Smithsonian Miscellaneous Collections, 65, No. 11, (1915.)
[5] Nature, 104, 661 (1920).
[6] Nature, 105, 71, (1920).
[7] Jour. Am. Chem. Soc., **39**, 880 (1917).

CHAPTER VIII

THE SO-CALLED NEGATIVE NATURE OF ATOMIC GROUPS OR RADICALS

It became apparent very early in the history of chemistry that the forces acting between the atoms could not be simple attractive forces like gravity. As has been pointed out, the analogy between chemical and electrical phenomena was observed and for a time received international recognition among chemists, but following the rise of the Type Theory the idea that chemical action involved an exchange of electricity was almost completely ignored. Nevertheless, even during the period when Kekulé's views were most in the ascendant, C. W. Blomstrand (1869) succeeded in weaving the threads of Berzelius' electrochemical theory into the very texture of the theories of Frankland, Kolbe and even of Kekulé. It is true that these developments commanded very little attention at the time, but a later generation appreciated the soundness of this classic work. Blomstrand's conception of diazonium salts as compounds which contain both trivalent and pentavalent nitrogen has for the past dozen years superseded the long prevailing views of Kekulé, and his writings contain the kernel of many other ideas which are of paramount importance to-day. It was Blomstrand who first expressed the idea that the carbon in —NC is bivalent, a fact which was later proven experimentally by Nef. In 1869, however, organic chemistry was, in general, impenetrable to electrochemical conceptions, and even such an original work as van't Hoff's "Ansichten über Organischen Chemie" was for many years entirely without influence upon theoretical developments in this field.

Yet even at this time certain specific relationships which exist between different atoms were manifest. It was known that a metallic atom coupled much more easily with oxygen than with carbon, and furthermore that in the condensation of hydrogen cyanide with aldehydes and ketones, the hydrogen always combined with oxygen and the cyanogen with carbon, and that the opposite arrangement was never observed. But while these and a large number of similar phenomena were noted, all attempts to explain them failed to reveal

fundamental causality. It must be confessed, however, that such atomic relationships are not always simple and may at times be very complex. In order to avoid misunderstanding in the course of the further development of this theme, it will be necessary, therefore, to pause at this point and to consider both the differences and the similarities which exist between the so-called negative nature of atomic groups and the electrochemical character of the elements.

Characteristic differences in the properties of saturated and unsaturated organic compounds, as well as such gradations in unsaturation as are observed in the case of ethylene and benzene derivatives, were first brought into prominence through the investigations of A. von Baeyer and his students. These researches were primarily concerned with the thermal relationships of these substances, but it soon became apparent that the influence of the unsaturated condition upon physicochemical properties was very general. A study of molecular volumes, electrolytic conductivity, and especially of molecular refractions all showed the same influences, acting always in the same direction and in conformity to natural and fundamental laws. It remained for F. Henrich [1] to demonstrate that all of the remarkable series of reactions, which had hitherto been referred to the so-called negative nature of certain radicals, were actually due to their unsaturated character.

When Victor Meyer [2] discovered the nitroparaffines, he observed that they were capable of forming salts with alkali, a phenomenon which could not at that time have been foreseen from theoretical considerations. Further investigation revealed the following regularity in the behavior of nitroparaffines up to nitro-butane. If one of two hydrogen atoms in union with carbon is replaced by a nitro group, the properties of the remaining hydrogen atom are affected in the sense that it becomes more acidic or negative in character and is now capable of being replaced by a metal. Similar observations were made in the case of ethyl acetoacetate and diethyl malonate,[3] and later in the case of nitrocinnamyl ketone and benzoyl acetone.[4] In these latter cases the remarkable behavior of the hydrogen of the methylene group was attributed to the influence of the organic radicals CH_3CO—, —$COOC_2H_5$, C_6H_5CO—, etc. New compounds were easily formed by treatment of these metallic derivatives with alkyl halides. Later it was discovered that these supposedly acid hydrogen atoms were

[1] Ber., **32**, 668 (1889); also Habilitationsschrift, Erlanger, 1900, Junge and Son.

[2] Ber., **5**, 404 (1872); Annalen der Chemie, **171**, 1 (1874); **175**, 88 (1875); **180**, 111 (1876).

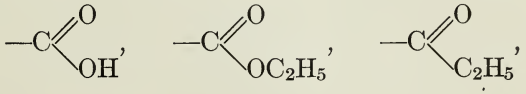
[3] Annalen der Chemie, **186**, 182 (1877).

[4] Ber., **16**. 33 and 2239 (1883); **18**, 2132 (1885).

capable of reacting not only with metals but with halogen, nitrous acid, aldehydes, salts of diazobenzene, etc. Thus on the basis of experimental evidence the rule governing the effect of nitro-substitutions was extended to include the substitution of other so-called negative groups and may be stated as follows: " if one of two or more hydrogen atoms in union with carbon is replaced by unsaturated groups such as $—NO_2$, $—COCH_3$, $—COC_6H_5$ and $—COOC_2H_5$ the remaining hydrogen atoms will show acid properties and increased chemical reactivity." [1] As the result of the researches of Haller, Held, Henry and others, the cyanogen group was subsequently added to this list.

The first systematic investigation of this problem was, however, undertaken by Victor Meyer in 1887, when he began the publication of his series of important papers on the " negative nature " of organic radicals.[2] He defined an acid radical as a salt-forming group, or, in other words, as a group capable of decreasing the basicity of amines, and he supplemented the list of those already mentioned by the addition of the phenyl and thionyl groups. At the same time he pointed out a difference in the action of different acid radicals upon methylene and methine hydrogen, cyanogen being, for example, decidedly more negative than carbethoxy $—COOC_2H_5$. Claisen has since shown that $—COCH_3$ and $—COC_6H_5$ are also more negative than $—COOC_2H_5$. Later vinylene, CH=CH,[3] came to be recognized as a negative group following the researches, dating from 1889 on, of von Baeyer,[4] W. Markwald,[5] Claisen [6] and F. Henrich.[7] The investigations of Thiele [8] on ethyl phenyl-acetoacetate and of W. Wislicenus [9] on indene and fluorene support this view.

The number of negative radicals continued to be increased as a result of investigation and came to include the following:



[1] Annalen der Chemie, **204**, 198 (1880).

[2] Ber., **20**, 534 and 2944; **21**, 1295, 1306, 1316, 1331, 1344, etc. (1888).

[3] Compare O. Hinsberg, Jour. prakt. Chemie, **84**, 180 (1911); **85**, 337 (1912).

[4] Annalen der Chemie, **251**, 267 (1889).

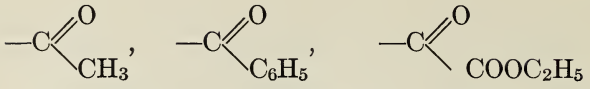
[5] Annalen der Chemie, **279**, 9 (1894); Ber., **28**, 1501 (1895).

[6] Annalen der Chemie, **297**, 14–16 (1897).

[7] Ber., **31**, 2103 (1898); **32**, 670 (1899); **33**, 668, 851 (1900); Monatsh. Chemie, **20**, 539 (1899).

[8] Annalen der Chemie, **306**, 114 (1899); Ber., **33**, 666, 851, 3359 (1900); **34**, 68 (1901).

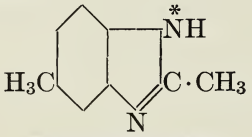
[9] Ber., **33**, 771 (1900).



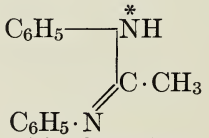
$$-NO,\ NO_2,\ -CH{=}CH-,\ {=}C{=}CX_2,$$
$$C{=}C,\ C{\equiv}N,\ -C_6H_5\ -C_{10}H_7\ \text{and}\ C_4H_3S.$$

These groups possess one characteristic in common, as was pointed out by F. Henrich in 1899, viz., they consist of multivalent atoms, whether of the same kind or of different kinds, which are bound together by means of double or triple bonds. That the negative character of the group varies with the degree of unsaturation of its atoms is shown by the strongly negative properties of NO_2 and $C{\equiv}N$. Further, the degree of unsaturation may be regarded as corresponding to a relatively high energy content, as shown by the heats of combustion, molecular refraction, etc., of the substances. According to Henrich it is not only characteristic of negative radicals, but essential to their very existence that they contain homogeneous or heterogeneous atoms in dense groupings, that is to say, bound together by double or triple bonds.[1]

If this statement is correct it should follow that all unsaturated groups possess negative properties, and this is in fact the case. Henrich has already pointed out that the group CH=N is negative in character, and that it is due to its influence that the hydrogen of the imido group, NH, in the following compounds for example, is replaceable by metals.

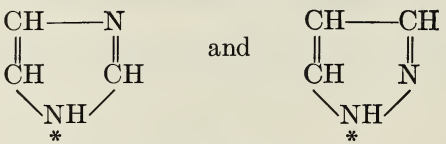


Dimethylbenzimidazol



Diphenylacetamidine

These substances and their derivatives have been investigated by Bamberger, Berle and Lorenzen. This acidic character of the NH group is not only observed in the acyclic and cyclic amidine combinations but also in the cyclic hydrazines, as represented, for example, by the following compounds where the imido hydrogen is readily replaceable by metals. It may be noted that the unsaturated grouping —CH=N functions in both classes of compounds.



[1] Ber., **32**, 673 (1899).

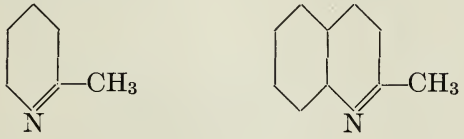
Bamberger and Berle [1] made the further discovery that dimethylbenzimidazol is capable of forming condensation products with aldehydes. A study of this interesting reaction revealed the fact that only one of the two methyl groups present in the molecule was able to react in this way. It was identified as the methyl group in direct union with the carbim radical (CH=N), the other methyl being entirely inert toward aldehydes. This marked difference in chemical activity was naturally interpreted as due to the influence of the negative group CH=N. The reaction thus becomes directly comparable to a normal ketone condensation,

$$\begin{array}{l} RCCH\cdot H_2 \\ \| \\ O \end{array} + OCH\cdot CH_3 \rightarrow \begin{array}{l} RCCH : CHCH_3 \\ \| \\ O \end{array} + H_2O$$

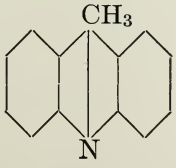
and may be expressed by means of the following equation:

$$\begin{array}{l} RCCH\cdot H_2 \\ \| \\ N- \end{array} + OCHCH_3 \rightarrow \begin{array}{l} RCCH : CHCH_3 \\ \| \\ N- \end{array} + H_2O$$

Similar condensations have been noted in the case of α-methyl pyridine and α-methyl quinoline and other cyclic combinations of similar structure,

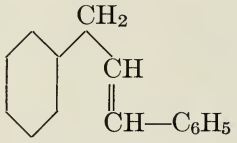


and may be interpreted as offering additional proof of the negative influence of the carbim group, —CH=N. The negative character of this grouping has also been strongly commented upon by E. Erlenmeyer, Jr.,[2] who in this way explains the tendency of hippuric acid to condense with aldehydes.[3] It has been observed that methyl groups in the γ position to nitrogen, as in methylacridine,



[1] Annalen der Chemie, **273**, 277 (1893).
[2] Jour. prakt. Chemie, **62**, 145 (1900).
[3] Annalen der Chemie, **337**, 219 (1904).

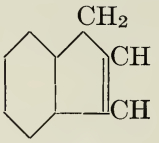
also show increased chemical reactivity and play the part of acidic or negative groups. Here we have complete saturation of the molecule, and consequently the increased reactivity cannot be explained in terms of the above hypothesis. It must be assumed to be due to other causes, as, for example, the very dense grouping of the atoms in the molecule [1] or to other molecular or structural influences which exert the same effect as unsaturation. In this connection it may be noted that dense groupings of the atoms, such as are common to the various types of ring structure, tend to produce increased chemical activity. A comparison of the following compounds demonstrates



Diphenylpropylene

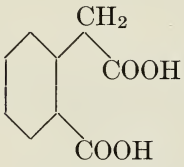
I

and



Indene

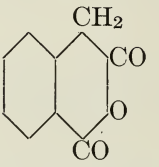
II



Homophthalic acid

III

and



Homophthalic anhydride

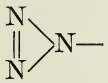
IV

according to W. Dieckman [2] that the closing of the ring materially increases the reactivity of the methylene group.

In 1894 Bamberger [3] pointed out the distinctly negative character of the azo group, N=N, in organic combinations. Thus in diazoamidobenzene and related compounds the imido groups possess weakly acid properties, but these are greatly strengthened by the introduction of nitro groups into the benzene nucleus. For example, the acidity of diazoamidobenzene is increased to such an extent by introduction of two nitro groups into the benzene nucleus that the resulting compound, $NO_2C_6H_4N{=}N \cdot NHC_6H_4NO_2$, dissolves even in weak alkali solutions to form salts. Still later O. Dimroth [4] was able to show that even diazo-amino compounds of the fatty series possess pronounced acid properties. The azo group is ordinarily only weakly negative in character. When, however, both of its free affinities, $-N{=}N-$, are

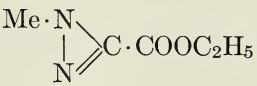
[1] Compare Ber., **39**, 3046 (1906).
[2] Ber. **39**, 3046 (1906); **47**, 1428 (1904).
[3] Ber., **27**, 2511 (1894).
[4] Ber., **39**, 3905 (1906).

satisfied by union with a common atom, as is the case in hydrazoic acid, HN_3, in which the azo group may be regarded as replacing two of the hydrogen atoms in ammonia, the atomic density of the grouping causes a marked increase in acid properties. In other words, the cyclic group,



is characterized by its strongly negative properties and is even capable of independent existence as an ion.

Th. Curtius [1] explained the action of metallic sodium and potassium upon ethyl diazoacetate by assuming that the hydrogen of the methine group is replaceable by metals with the formation of carbonium salts. A. Hantzsch [2] has shown, however, that this interpretation is incorrect, and that the ethyl diazoacetate reacts in its tautomeric form with metals giving nitrogen salts of the general formula:



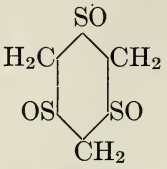
The reactivity of the imido hydrogen in this case may be interpreted as due in part to the influence of the double bond between the carbon and nitrogen (carbim grouping), and in part to the dense grouping of atoms in the molecule which results from ring formation.

The negative character of the group SO_2 in organic combination (sulphone) has been the subject of extended investigation. It was originally regarded as a negative radical and was included among the so-called negative groups by Haller. Later Victor Meyer pointed out that phenyl benzyl sulphone, $C_6H_5SO_2CH_2C_6H_5$, shows none of the reactions typical of the ketone $C_6H_5 \cdot CO \cdot CH_2 \cdot C_6H_5$, and for a long time after this the sulphone grouping (SO_2) ceased to be included in the list of acid radicals. In 1899, however, Michael [3] succeeded in demonstrating the reactivity of the methylene group in phenylsulphonic acid esters, as is represented in $C_6H_5SO_2 \cdot CH_2COOC_2H_5$. In the same year Autenrieth and Wolff,[4] and a year later A. Kotz [5] pointed out the mobility of hydrogen in cyclic sulphones possessing the atomic grouping,

$$—SO_2 \cdot CH_2 \cdot SO_2—$$

[1] Ber., **17**, 956 (1884); Jour. prakt. Chemie, **38**, 410 (2), (1888).
[2] Ber., **34**, 2508 (1901); **45**, 1657 (1912).
[3] Jour. prakt. Chemie, **60**, 96 (1899).
[4] Ber., **32**, 1381 (1899).
[5] Ber., **33**, 1120 (1900).

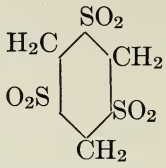
The reactivity of the methylene hydrogen in the following combinations



Trimethylene trisulphoxide

I

and



Trimethylenetrisulphone

II

is shown by the fact that both substances are distinctly acidic in character. The former is soluble in aqueous sodium hydroxide. It also reacts with aldehydes, diazo compounds, etc. The latter is a stronger acid and dissolves readily in sodium carbonate, but does not react with aldehydes, etc.[1]

It has already been observed that methylene hydrogen is more strongly influenced by such groups as CH=CH and COCH=CH than by C_6H_5; and it now appears that *o*-carbethoxyphenyl $C_2H_5OOC \cdot C_6H_4$— also belongs to the former class. This follows from the researches of Dieckmann,[2] who has discovered that homophthalic ester reacts readily with benzylbromide in the presence of potassium ethoxide to give benzylhomophthalic ester:

$$C_2H_5OOC \cdot C_6H_4 \cdot \underset{\displaystyle CH_2C_6H_5}{\underset{|}{CH}} \cdot COOC_2H_5$$

and with benzaldehyde in the presence of sodium ethylate to give benzalhomophthalic acid

$$HOOC \cdot C_6H_4 \cdot \underset{\displaystyle CH \cdot C_6H_5}{\underset{\|}{C}} \cdot COOH$$

Dieckmann has pointed out in this connection that this observed reactivity of the CH_2 group is in marked contrast to the behavior of this group in ethyl phenylacetate.

Further generalizations along these lines have resulted from the investigations of D. Vorländer,[3] who calls attention to the fact that the acid character of the hydrogen atom present in the carboxyl group of acids is not due to the influence of either —CO or —OH alone, but

[1] Hinsberg, Jour. prakt. Chemie **85**, 337, 351 (1912).

[2] Ber., **47**, 1428 (I914).

[3] Abhandlungen der naturforschen Gesellschaft zu Halle, **21**, 235 (1899); Ber., **34**, 1632 and 1637 (1901); Annalen der Chemie, **320**, 66 and 99 (1901).

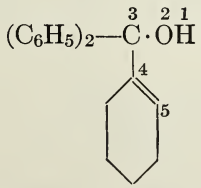
to the combined influence of both groups. If the symbol E be made to represent a non-metallic element, then the expressions

$$\underset{1\ 2\ 3\ 4}{H\cdot E\cdot E{=}E}; \qquad \underset{1\ 2\ 3\ 4}{H\cdot E\cdot E{\equiv}E}; \qquad \underset{1\ 2\ 3\ 4}{H\cdot E{=}E{=}E}$$

represent the atomic groupings common to most organic and inorganic acids. Vorländer calls the unsaturated atoms occupying positions 3–4 the reactive group, and points out that this group is both physically and chemically active. The mobility of the hydrogen in any such complex depends (1) upon the nature of the non-metallic atom with which the hydrogen is in direct union, and (2) upon the nature and relative degree of unsaturation of the non-metallic atoms 3 and 4. In order to increase the mobility of hydrogen above that observed in the types HCl, H_2O, H_2S, NH_3 and CH_4, a double bond must be introduced in the position 3–4. This is shown, for example, by the strongly acid properties of such compounds as chloric acid $O{=}\overset{OH}{\overset{|}{Cl}}{=}O$ and hydroxamic acid $HO\cdot N{=}\overset{OH}{\overset{|}{C}}\cdot R$. A " reactive group " in other positions, as in the combinations

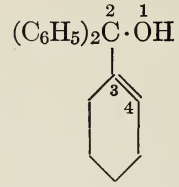
$$\underset{1\ 2\ 3}{H\cdot E{=}E} \qquad \text{and} \qquad \underset{1\ 2\ 3\ 4\ 5}{H\cdot E\cdot E\cdot E{=}E}$$

has no influence upon the mobility of the hydrogen. This is obvious from a consideration of the chemical properties of aldehydes, chloral hydrate, and also from a study of the behavior of triphenylcarbinol. It has been observed, for example, that the hydroxyl group in the latter compound is no more strongly acidic than in the aliphatic alcohols. The fact that the presence of three strongly negative groups do not increase the acidity of this substance may be explained by reference to the following structural formula:



when it becomes apparent that the hydrogen atom occupies an unfavorable position with reference to the unsaturated vinylene groups. The fact that this substance differs from the aliphatic alcohols in its ability

to split off hydroxyl and so to exhibit basic properties is explained by Vorländer [1] as due to the favorable position of the oxygen:



It may be added that the mercapto group in triphenylthiocarbinol shows a similar tendency to undergo analogous changes.

Vorländer explains the fact that nitrogen bases are readily oxidized in alkaline and not in acid solution, by supposing that the free bases are unsaturated compounds while their salts are saturated. Trivalent nitrogen thus belongs to the same general category as C=C, C=O, etc., and the following pairs of reactions may be regarded as strictly analogous in character:

$$R_3N{=}{+}HBr \rightleftarrows R_3N\begin{cases} H \\ Br \end{cases}$$

$$R_2C{=}CR_2{+}HBr \rightleftharpoons R_2\underset{\displaystyle H}{\underset{|}{C}}{-}\underset{\displaystyle Br}{\underset{|}{C}}R_2$$

$$H_3N{=}{+}H_2O \rightleftharpoons NH_4OH$$

$$CCl_3CH:O{+}H_2O \rightleftharpoons CCl_3\cdot CH(OH)_2$$

Thus the relative reactivity of the nitrogen is measured by the basicity of its compounds. The analogy is complete when the influence of trivalent nitrogen upon the mobility of hydrogen is considered. This is the same as in the case of ethylene, as may be seen from a comparison of the following formulas:

$$\underset{1}{H}\cdot\underset{2}{E}\cdot\underset{3}{E}{=}\underset{4}{E} \quad \text{and} \quad \underset{1}{H}\cdot\underset{2}{E}\cdot\underset{3}{N}{=}$$

I II

in both of which hydrogen occupies the favorable 3-position with reference to the unsaturated element.

Many phenomena observed in the oxidation of amines may be explained on the basis of these assumptions. Thus ammonia NH_3, azobenzene $C_6H_5N{=}NC_6H_5$, and similar substances are very stable in the presence of oxidizing agents, while aliphatic amines, CH_3NH_2

[1] Ber., **46**, 3450 (1913).

hydroxylamine NH_2OH, hydrazine and similar combinations are readily oxidized. Although substances belonging to the first class of compounds contain reactive nitrogen, this is not in a position to affect the mobility of the hydrogen atom. Substances belonging to the second class of bodies, on the other hand, contain the combination H·E·N:, and, according to Vorländer, should therefore be reactive.

Two ethylhydroxylamines are theoretically possible according to whether the alkyl group is attached to oxygen or nitrogen, i.e.,

$$C_2H_5O\cdot\overset{\|}{N}H_2\ (\alpha) \qquad \text{and} \qquad HO\overset{\|}{N}H\cdot C_2H_5\ (\beta)$$

Of these the former should be stable and the latter unstable toward oxidizing agents. In 1880 Gorke[1] was able to show that α-ethyl hydroxylamine is not attacked even by boiling alkali solutions of copper, while its isomer reduces Fehling's solution in the normal way. Aniline, $C_6H_5\cdot NH_2$, and dimethyl aniline, $C_6H_5\cdot N(CH_3)_2$, on the other hand, are both readily oxidized since both contain hydrogen in the correct structural relation to an unsaturated group, as is represented by the following expressions

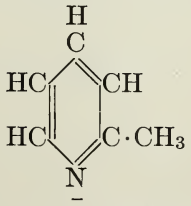
$$H_2N\cdot\overset{|}{C}=\overset{|}{C}— \qquad \text{and} \qquad (CH_3)_2\overset{\|}{N}\cdot C_6H_5$$

respectively. The following pairs of substances also show marked analogy in their chemical properties:

$$(CH_3)_2N\cdot C_6H_5 \qquad \text{and} \qquad CH_3\overset{\|}{C}\cdot C_6H_5 \quad (\overset{\|}{O})$$

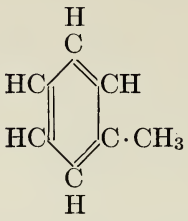
$$C_6H_5NH\cdot CH_2COOH \qquad \text{and} \qquad C_6H_5\overset{\|}{C}\cdot CH_2COOH \quad (\overset{\|}{O})$$

The unsaturated character of nitrous acid is shown by the ease with which it passes into nitric acid on oxidation with permanganates. Sodium nitrite and amyl nitrite, on the other hand, resist oxidation because they possess no mobile hydrogen. Vorländer explains the fact that the methyl group in α-picoline,



[1] Annalen der Chemie, **205**, 277 (1880).

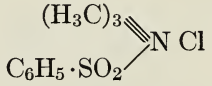
is distinctly more reactive than in toluene,



by assuming that the former compound contains unsaturated nitrogen. In toluene the carbon atoms of the benzene ring exercise their maximum valency.

The addition of the unsaturated elements, nitrogen, oxygen, and sulphur,[1] to the general category of unsaturated (i.e., so-called negative) groups, affords a new point of contact between organic and inorganic chemistry. Vorländer is of the opinion that the same general relations hold between saturated and unsaturated compounds, whether organic or inorganic and whether compounds of the positive metals or of the negative non-metallic elements.

It should be added that Vorländer has succeeded in demonstrating experimentally that one and the same radical may be positive or negative in character, depending upon the form of chemical combination in which it is found. He even shows that the effect of a so-called negative radical may be to strengthen instead of weaken the basic properties of a given compound. For example, Vorländer and Nolte [2] have recently discovered that trimethylamine will combine with benzene sulphonchloride to give a salt-like body. The product is neutral in aqueous solution and may be readily separated in the form of the chlorplatinate. Analysis shows that it is formed by the addition of one molecule of benzene sulphonchloride to one molecule of trimethylamine, and it is regarded by Vorländer and Nolte as representing the first member of a new type of quaternary ammonium salt in which the acid radical $C_6H_5SO_2$— takes the place of an alkyl residue, viz.,



[1] Hinsberg, Ber., **43**, 901 (1910); Jour. prakt. Chemie, **84**, 184 (1911); Pummerer, Ber., **43**, 1376 (1910).

[2] Ber., **46**, 3215 (1913).

Now, benzensulphonic acid is even more strongly acidic than sulphuric acid and it would, therefore, seem reasonable to expect such a strongly acid residue as $C_6H_5SO_2$— to decrease the stability of the resulting compound. As a matter of fact, this salt is not hydrolyzed by water. It is acted upon by moist silver oxide with the formation of the free base which then undergoes immediate decomposition.

These facts would seem to indicate that the salt-forming and essentially basic properties of ammonia are not entirely destroyed by the introduction of a negative group like $C_6H_5SO_2$— into the so-called ammonium complex. In such a case as this, where a distinctly negative group does not function in a negative manner, it becomes necessary to reconsider the whole matter, if possible, from a different angle. According to Vorländer and Nolte, the fact that ammonia, aniline, nitraniline and diphenylamine show differences in their ability to form bases by the addition of water, and salts by the addition of acids, may be explained upon the assumption of differences in what they call the *aminity* of the substances and not of differences in their basicity. The degree of *aminity* depends upon the unsaturated character of the nitrogen atom and not primarily upon the positive or negative character of the groups in union with it. In other words the ordinary conception of strong and weak ammonia bases[1] must be abandoned, and the strength of a given amine must be measured in terms of the free affinity of its nitrogen as expressed in the ability of the substance to enter into addition reactions.

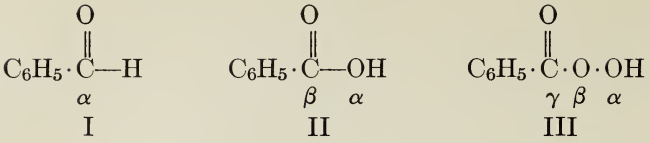
In applying this idea to radicals containing multivalent elements other then nitrogen, Vorländer assumes the existence of a "dual nature" which depends primarily upon the positive or negative character of the element in question and secondarily upon the saturated or unsaturated condition of the molecule in which that element is found.[2] The facts may be briefly summarized by saying that the reactivity of the hydrogen present in —OH, NH, CH, etc., depends upon the presence of unsaturated atoms or groups in favorable positions.

The conceptions of Henrich and Vorländer have recently been extended by O. Hinsberg[3] as the result of a study of ionization phenomena. A comparison of the chemical properties of the three types of compounds represented by formulas I, II and III,

[1] Jour. prakt. Chemie, **87**, 90 (1913).

[2] Compare Vörlander, Ber., **37**, 1646, 1651 (1904). Annalen der Chemie, **341**, p. 1 and following; **345**, 155, 251 (1906).

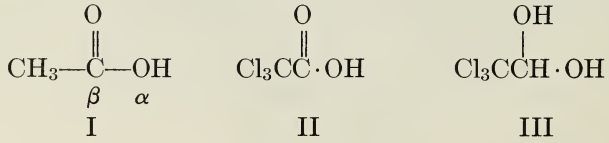
[3] Jour. prakt. Chemie, **84**, 169 and following (1911): A more recent treatment in Jour. prakt. Chemie, **85**, 337 (1912) is valueless at present.



I II III

leads to the discovery of striking differences in behavior. While all three possess reactive hydrogen, the influence of the carbonyl group on the hydrogen atoms in the α, β and γ positions respectively is markedly different. Thus the hydrogen present in I is non-ionizable and is not replaceable by metals. It is, however, capable of being replaced by Cl, $O \cdot COCH_3$, etc., and its reactivity is stimulated by the presence of potassium cyanide. The hydrogen present in II and III, on the other hand, shows distinctly acid properties, III being a very weak acid whose salts are decomposed by carbon dioxide and II being so decidedly acid as to show ionizable hydrogen. Thus the carbonyl group is capable of acting in two ways: it may simply intensify the mobility of the hydrogen atom so that the usual reactions take place more readily as, for example, in the case of I, or it may act to change the character of the hydrogen so that it is no longer capable of the usual reactions but exhibits typically acid properties, as in II and III. In general it has been found that other unsaturated groups, in the α, β and γ positions respectively, exercise the same influence upon hydrogen as the carbonyl group. The rule is not perfectly general, however, since certain atoms in the α position are capable of bringing about the ionization of hydrogen, as for example, Cl in HCl and S in HSH. Hinsberg classifies such atoms as Ionogens of the First Order, while atoms and groups in the β position are classified as Ionogens of the Second Order.

A comparison of the properties of the three organic substances represented below shows that the acid hydrogen atom in II is much more strongly ionized than that in I by the presence of carbonyl in the β position:



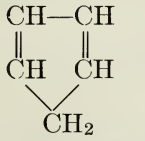
I II III

This marked difference in properties is obviously due to the substitution of chlorine in the methyl radical, but that this does not wholly explain the phenomenon is shown by the fact that chloral hydrate,

III, is neutral in its properties. The primary condition for the ionization of hydrogen thus seems to be the presence of the carbonyl group in the β position. If such an unsaturated group is present in the molecule chlorine may exercise a secondary influence by increasing the degree of ionization. Hinsberg has formulated these facts as follows: Ionogens of the first order have an acidifying influence upon hydrogen atoms present in organic molecules only when these are simultaneously acted upon by ionogens of the second order.

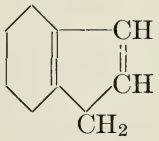
If the acidity of a substance is increased by the presence of certain groups in its molecule, it should also be possible to decrease the negative properties or even to change the whole character of the substance from acidic to basic by the introduction of other groups. This is in fact true as the following example shows: sulphur may be assumed to possess originally only negative ionogen valencies, since its hydrogen derivative, H_2S, is a weak acid. If sulphur is in union with three methyl groups, however, its character is completely changed from acidic to basic, and the resulting trimethyl sulphonium radical $(CH_3)S_{3'}\sim$, is found to possess one positive ($\sim$) ionogen valence. Hinsberg calls such radicals " commuting groups " (" Kommutierende Atomgruppen ") and defines them as groups which strengthen or weaken ionogen valencies without being able themselves to create such valencies.

The behavior of the unsaturated vinylene group, —CH=CH—, is very remarkable in that it seems to have the power of acting in two capacities, viz., it is capable of bringing about the ionization of hydrogen atoms occupying the β position with reference to it, in the sense of forming either cations or anions. Thus, for example, it evidently plays the rôle of a *negative* ionogen of the second order in both cyclopentadiene and indene,



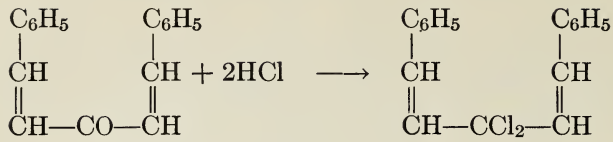
Cyclopentadiene

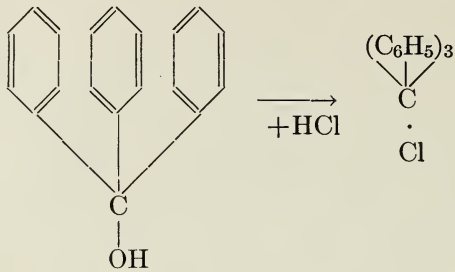
and



Indene

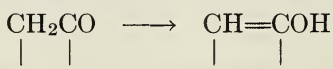
since the hydrogen of the methylene group is very reactive in both of these substances. On the other hand, it functions as a *positive* ionogen of the second order when occupying the β position with relation to such anions as Cl, $—OSO_3H$, $—ONO_2$, etc. The basic character of the following oxide and hydroxide is clearly demonstrated by their ability to form salts in which the anion, chlorine, is in the β position to two or more vinylene groups:



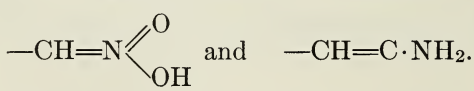


These apparently opposite functions of the vinylene group may be readily interpreted in terms of Vorländer's theory in regard to the dual nature of radicals.[1]

Ionogens of the second order not only exercise an acidifying influence upon hydrogen but may affect its reactivity in other ways. Thus, for example, if the presence of an ionogen increases the tendency of a substance to undergo intramolecular rearrangement in the sense



it is obvious that the reactivity of the hydrogen will be indirectly affected. That the *enol* modification is in fact more reactive than the corresponding *keto* form has been demonstrated experimentally by Kurt H. Meyer [2] who has shown that it alone is capable of entering into reactions with aldehydes, nitrous acid, diazo and nitroso compounds. The groups $—CH_2NO_2$ and $—CH_2CH{=}NH$ show a similar tendency to rearrange into the more reactive atomic groupings

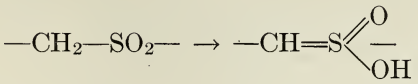


If this conception is correct and ionogens actually do, in some cases, induce intramolecular rearrangements, it would serve to explain the somewhat remarkable relationships observed in the case of trimethylenetrisulphoxide and trimethylenetrisulphone. It may be recalled that of these two substances the latter is more strongly acid than the former but does not react with aldehydes, diazo compounds, etc. This

[1] A. Kotz, "Betrachtungen über die Reaktivität schwefelhaltiger Atomgruppierungen." Nernst-Festschrift, bei W. Knapp in Halle, p. 227.

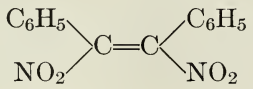
[2] Annalen der Chemie, **379**, 37 (1911); **380**, 212 (1911)

is explained by Hinsberg,[1] who supposes that rearrangements in the sense



do not take place readily and that quite specific conditions are necessary in order to bring them about.

It has been observed that under different conditions one and the same group may function in either of two diametrically opposite ways. The reenforcing or activating influence of the phenyl group has already been referred to, but that phenyl does not always function in this way is seen from the fact that the presence of a number of phenyl groups in union with ethylene carbon may actually retard addition to the ethylene bond. For example, tetraphenyl-ethylene does not react with bromine despite the fact that it contains an unsaturated double linkage. This is also true of dinitrodiphenyl-ethylene.[2]



The character of both of these substances is, however, such that it is difficult to say whether this effect is due to the chemical nature of the substituents or to stereochemical influences.[3] In order to decide this question, H. Biltz [4] prepared a number of substances in which the phenyl groups in union with the ethylene carbon atoms were replaced by halogen atoms. His results were not conclusive, although he was able to show that while unsaturated compounds heavily loaded with halogen will still add halogen, they react much less readily than when not so laden.

Other experiments which have been undertaken with the same end in view have given equally equivocal results. For example, Emil Fischer and G. Giebe [5] discovered that acetals could readily be prepared according to Fischer's esterification method [6] by treating aldehydes with 1 per cent hydrochloric acid in alcohol solution.

$$C_6H_5CHO+2HOC_2H_5 \rightarrow C_6H_5CH(OC_2H_5)_2+H_2O$$

[1] Jour. prakt. Chemie, **85**, 351 (1912).

[2] J. Schmidt, Ber., **34**, 619 (1901).

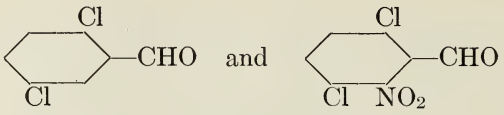
[3] J. Schmidt, "Ahrens Samml. Chem. und Chem. Techn. Vortrage," 7, vols. 9 and 10 (1902).

[4] H. Biltz, Annalen der Chemie, **296**, 231, 263 (1897).

[5] Ber., **34**, 619 (1901).

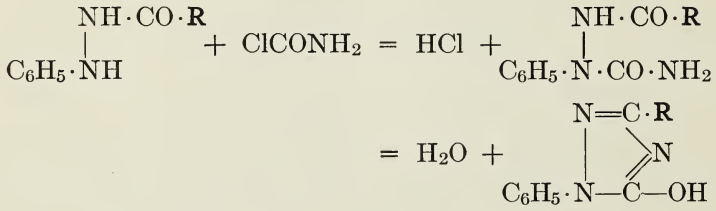
[6] Fischer, Ber., **30**, 3053 (1897).

In applying this reaction to substituted aromatic aldehydes they found that *o*-nitrobenzaldehyde reacted to form the corresponding acetal with greater ease than did benzaldehyde itself.[1] This was also true in the case of the following substituted aldehydes:

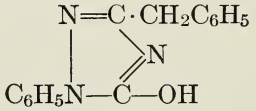


In other words, electro-negative substituents, although in the *ortho*-position and of high molecular weight, accelerate the reaction.[2] This is exactly the opposite of what might be expected, at least in the case of mononitrodichlorbenzaldehyde on the basis of Victor Meyer's law of esterification as applied to acids.

Recent experiments by Rupe and Labhardt do, however, seem to show in a fairly conclusive manner that the relatively great extension of phenyl groups in space does not in itself affect the reactivity of adjacent carbonyl linkages. These investigators have prepared phenyloxytriazoles by treating β-acylphenylhydrazines with carbamyl chloride:



In applying this reaction to a great number of cases they discovered that triazoles were formed only when the radical R was not unsaturated or, in the old sense, *negative*. For example, no triazole could be obtained in which R equals —C_6H_5 although the corresponding C_7H_7



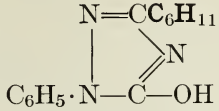
compound could be prepared.

In order to determine whether the extension of the phenyl group in space interferes with the formation of diphenyloxytriazole, Rupe and Metz investigated the action of carbamyl chloride upon β-hexa-

[1] Ber., **31**, 545 (1898).

[2] H. Biltz, Annalen der Chemie, **296**, 231, 263 (1897).

hydrobenzoylphenylhydrazine. In this case the reaction proceeds smoothly and 1-phenyl 3-hexahydrophenyl-5-oxytriazole

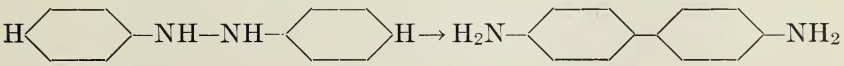


is formed. This result would seem to eliminate any explanation of the phenomenon based upon steric hindrance, since a triazole in which R equals $—C_6H_{11}$ can be prepared, although the corresponding compound in which R equals $—C_6H_5$ cannot. It would therefore seem to follow that the reaction is actually inhibited by the unsaturated character of the phenyl group. This conclusion is sustained by the results obtained in a series of experiments in which R equals $—CH_2CH_2CH_3$, $—CH{=}CH \cdot CH_3$, $—CH_2CH_2C_6H_5$, $—CH{=}CH\ C_6H_5$ and where the observed decrease in the reactivity of the hydrazine corresponded to the degree of unsaturation of the radical.

In the process of acetylating amines [1] the effect of electro-negative groups is directly opposite to that in the instances just mentioned. The relations are, however, more complicated, and it has been observed that substituents in the *ortho* and *para* positions behave differently.

In the following pages a number of illustrations will be given to show the way in which some of the more important so-called negative groups function under different conditions and in different forms of combination.

A very exact investigation by P. Jacobson and his students,[2] in regard to the influence exercised by various substituents in determining the course of intramolecular rearrangements among the aromatic hydrazines, has led to the discovery of a number of interesting facts. If hydrogen is present in both *para*-positions of the benzene ring diamido-diphenyl derivatives (the so-called benzidine bases) result, as is represented by the following equation:



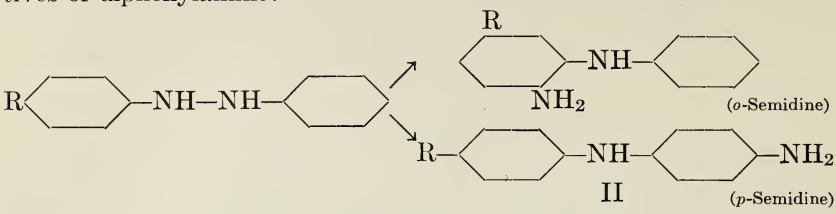
I

If, however, either one of these positions is occupied by some other substituent than hydrogen, the course of the transformation is altered,

[1] Ber., **27**, 93 (1894).

[2] Ber., **25**, 992; **26**, 681, 688, 699; **27**, 2700; **28**, 2541; **29**, 2680; **31**, 890; **36**, 3841, 3857, 4069, 4093; Annalen der Chemie, **287**, 97 (1895); **303**, 290 (1898).

and the main products of the reaction are now monoamido derivatives of diphenylamine:



In this case, side reactions also take place resulting in benzidine rearrangements and in decompositions into monamines. Indeed, in the reduction of azo-compounds by means of zinc and hydrochloric acid, all of these processes may take place simultaneously as, for example, in the case of chlorazobenzene. In general it may be said that the character and amount of the reaction product in any given instance depends upon the chemical nature of the substituent and also upon its relative position in the molecule. Jacobson determined the influence of nine substituents in the *p*-position, namely, Cl, Br, I, $—OC_2H_5$, $—OCOCH_3$, $—N(CH_3)_2$, $—NHCOCH_3$, $—CH_3$ and —COOH.[1] His results show that substitution of hydrogen in hydroxyl or amido groups in the *para*-position to the azo group by alkyl or acyl radicals has a very marked effect upon the course of the rearrangement. If hydrogen is replaced by an alkyl group as, for example, in *p*-ethoxyhydrazobenzene, rearrangement takes place exclusively in the sense of II and semidine is formed, the presence of the alkyl group being unfavorable to diphenyl rearrangement as in I. The reverse happens if the hydrogen of hydroxyl is replaced by acetyl as in *p*-acetoxyhydrazobenzene, where a diphenyl base forms the principal product of rearrangement. In general it may be said that alkyl and acyl groups produce directly opposite effects in influencing rearrangements of this type. Such rearrangements are not always in the sense which has just been described, however. Thus, while in the case of derivatives of *p*-hydroxyazobenzene, alkyl groups favor semidine and acyl groups favor diphenyl rearrangements, the reverse holds in the case of derivatives of *p*-amidoazobenzene, where the presence of alkyl groups favor diphenyl and acyl groups semidine rearrangements. Free amido- and hydroxyazo-compounds do not themselves rearrange, but decompose with the formation of two amines.

The effect of the substituents CH_3, Cl, Br, I is not so specific nor so definite as is the case with $—OC_2H_5$, $—OCOCH_3$, $—N(CH_3)_2$

[1] Annalen der Chemie, **303**, 296 (1898).

and —$NHCOCH_3$. The presence of a methyl group in the *para*-position seems to favor simultaneously both semidine and diphenyl rearrangement. Furthermore, it has been demonstrated with certainty that halogen derivatives of hydrazobenzene show approximately the same inclination to semidine as to diphenyl rearrangement.

It frequently happens that in the course of these rearrangements the substituent group R becomes detached from the aromatic nucleus. A study of this phenomenon shows that the substituents which are most firmly bound to the benzene ring are —OC_2H_5, —CH_3, —$N(CH_3)_2$ and —$NHCOCH_3$. This is shown by the fact that these four groups are not split off in the course of rearrangements. This stands in marked contrast to the behavior of —$OCOCH_3$, —COOH, Cl and Br, which separate with more or less ease. Indeed the group—$O \cdot COCH_3$ is so unstable that, in the reduction of acetoxyazobenzene in the presence of zinc and hydrochloric acid, the formation of acetic acid proceeds more rapidly than does the true reduction reaction. It is interesting to note that, although free hydroxy-azobenzene might be expected to rearrange to give a benzidine base, specially conducted experiments have shown that no trace of benzidine is formed, while the acetyl derivative under identical conditions gives considerable quantities of this compound. The conclusion follows that it must be the specific influence of the negative acetyl group upon the oxygen of the hydroxyl so weakens the affinity for oxygen for carbon of the benzene ring, that hydrolysis can be brought about under the extremely mild conditions of an experiment which takes place at a temperature below 40° C.[1]

An observation of F. Kehrmann [2] referring to the transformation

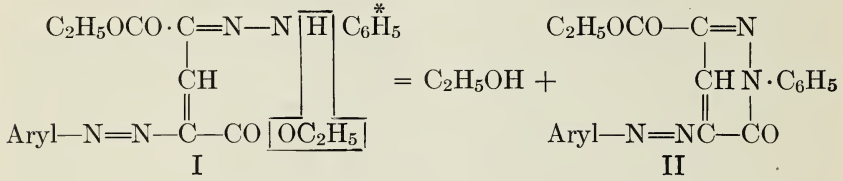
$$\underset{\text{Quinone}}{C_6H_4O_2} \rightleftarrows \underset{\text{Hydroquinone}}{C_6H_4(OH)_2}$$

is of especial interest in this connection, and may be stated as follows: the lower the homologue and the more negative the substituents in the molecule, the more easily quinones take up hydrogen and pass into hydroquinones, while the reverse reaction involving oxidation is favored by high molecular weight and by an accumulation of positive groups. This explains why a mixture of hydrothymoquinone and benzoquinone rearranges to give thymoquinone and hydrobenzoquinone, and why, as has been observed by C. Graebe, tetrachlorhydroquinone is oxidized at the expense of thymoquinone, giving chloranil

[1] Annalen der Chemie, **303**, 300 (1898).
[2] Ber., **31**, 979 (1898).

and trichlorhydroquinone. Hydroxyhydroquinone and aminohydroquinone are oxidized by the oxygen of the air with such energy that it is difficult to prepare them. Yet the corresponding acyl derivatives are usually stable, since the positive character of the —OH and —NH_2 groups is decreased by substitution of the negative acyl radical. Thus, for example, 4-amino-1, 2-hydronaphthaquinone, one of the most unstable substances of this class, gives an acetyl derivative which is stable in the air. Moreover, while pyrocatechol is stable in the air, β-hydronaphthoquinone oxidizes slowly and hydrophenanthroquinone oxidizes rapidly to the corresponding quinones upon standing in the air.

The researches of F. Henrich [1] throw further light upon this general problem. Henrich found that the hydrazone of benzazoglutaconic ester, which is formed from diazobenzene and glutaconic ester, splits off alcohol more or less readily and passes into a 1-2-diazine derivative (pyridazone):



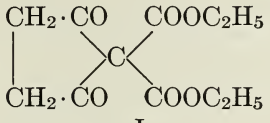
The relative ease with which this type of reaction takes place was observed to depend upon both the chemical nature of the substituent and upon its relative position in the benzene ring. Thus negative groups such as Cl, Br, NO_2, etc., in the *meta-* and *para*-positions accelerate the reaction.

After Kurt H. Meyer and Lenhardt [2] had made the surprising discovery that phenol ethers possess the same ability as phenols to couple with diazo compounds and thus to form the corresponding oxyazoethers, they proceeded to investigate the influence of substituents upon this type of reaction.[3] Results show that mono- and di-nitrodiazobenzenes couple much more energetically than azobenzene itself and that this is also true of the diazo derivatives of the halogenated anilines. In brief, " the more negative the substituent in the diazo compound the more readily do these compounds react with the phenol ethers." On the other hand, negative substituents in the phenol ethers produce the opposite effect and tend to retard the reaction. For

[1] Annalen der Chemie, **376**, 131 (1910).
[2] Annalen der Chemie, **398**, 74 (1913).
[3] Ber., **47**, 1741 (1914); also Auwers, Ber., **47**, 1275 (1914).

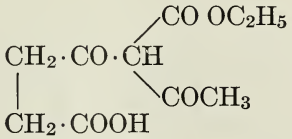
example, *p*-nitroanisol, and also nitro, sulphonic acid, and carboxyl derivatives of naphthol ethers either fail to couple or else react much more slowly than the corresponding unsubstituted ethers.

The sodium salt of diethylmalonate, when treated with succinyl chloride, interacts according to Schreiber to give a derivative of cyclopentane of the formula:



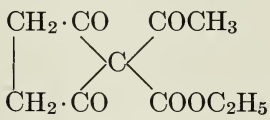
I

In other words, both acyl groups of the succinic acid link themselves to the methylene group in diethylmalonate. When, however, this investigator [1] modified the reaction by substituting the sodium salt of ethyl acetoacetate for the sodium salt of diethylmalonate, he obtained an acyclic or open chain compound, namely ethyl succinyl acetoacetate,



II

and all attempts to transform the latter compound into the corresponding pentane derivative,



III

by the elimination of water were unsuccessful. The stability of the compound I as compared with II and III affords another illustration of the disintegrating influence of the more negative acetyl group when substituted for the less negative carbethoxy group.

Brojendra Nath Ghosh [2] has recently published a very interesting article in which he points out the important influence which constitution has upon the basicity of oxygen. According to the observations which he has made, it would seem as if compounds which contain one or more oxygen atoms in a ring are very much influenced in their

[1] Ber., **44**, 2423 (1911).

[2] Jour. Chem. Soc., **107**, 1588 (1915).

ability to form salts with acids by the unsaturated or negative character of the substituent groups.

Many other illustrations might be mentioned.[1] In fact it may be said that a majority of the reactions in organic chemistry show either the restraining or accelerating influences of negative as compared with positive radicals. The subject will be considered again later from a somewhat different angle in the chapter on Tautomerism and Desmotropism. Every important reaction should be systematically studied from this point of view.

The term " negative radical " has undoubtedly merely an historical significance as applied to the various groups which have just been considered. In other words, this term no longer exactly expresses the condition which it attempts to describe. Because of this fact Vorländer has suggested the substitution of the term " reactive group " to express the condition represented by the unsaturated elements 3–4 in the atomic complex.[2]

$$\underset{1}{H}\ \underset{2}{E}\ \underset{3}{E}{=}\underset{4}{E}$$

Vorländer has also urged the use of the term " reactive influence " (" reaktive Wirkung ")[3] to describe action of an accelerating or disintegrating nature. Jacobson and Stelzner,[4] on the other hand, think that the term *reactive group* may be more suitably aplied to that part of a molecule (methylene group, for example) whose chemical reactivity is actually increased by the introduction of a given substituent. They further suggest that the terms *reenforcing* or *activating group* (" reaktivierende Gruppe ") and *reenforcing* or *activating influence* (" reaktivierende Wirkung") be used instead of the corresponding expressions, negative group and negative influence.

Since, however, unsaturated atoms or groups of atoms exercise a reenforcing influence only when they occupy certain definite positions in the molecule, as typified, for example, in the systems,

$$\underset{1}{H}\ \underset{2}{E}\ \underset{3}{E}{=} \qquad \text{and} \qquad \underset{1}{H}\ \underset{2}{E}\ \underset{3}{E}{=}\underset{4}{E}$$

it may be assumed that this whole complex is actually responsible for the increased chemical reactivity of the given part and that, there-

[1] Wieland, Habilitationsschrift, p. 9, Munich, V, Hoflung, 1904.

[2] Ber., **34**, 1633 (**1901**).

[3] Annalen der Chemie, **320**, 112 (1902).

[4] V. Meyer and Jacobson's " Lehrbuch der Organischen Chemie," 2nd Ed., vol. 1, 419.

fore, the term *reactive group* applies to the system as a whole, the hydrogen atom itself being simply " replaceable."

All of the rules which have been mentioned thus far as governing the action of unsaturated groups, are purely empirical in character. They lead directly to the assumption that in all cases the reactivity of the hydrogen atom is due to the presence of a given atom or radical in the molecule. The question as to the mechanism of the change involves a consideration of the phenomena of tautomerism, desmotropism and molecular rearrangements, so that its detailed discussion must be omitted for the present.

In conclusion it may be said that so equivocal are the terms *positive* and *negative* that Vorländer recommends that they should never be used except in cases where they are employed to describe the nature of the chemical elements themselves. Even when applied to individual chemical atoms, these terms must be used with discretion since many elements may appear to be positive under certain conditions and negative under others. Ordinarily the positive or negative character of a given element can be determined approximately from its position in the periodic system, from the basic or acidic properties of its respective oxygen and hydrogen derivatives, and from its electrochemical behavior. In certain instances where an element appears to be positive at one time and negative at another, it has been observed that the variation in these properties seems to depend upon its degree of saturation. For example, the exercise of its higher valencies often tends to make a metal appear more negative, and a non-metal more positive. Under these conditions there is obviously no sharp line of demarcation between these two groups of elements.

Vorländer [1] assumes that potential differences actually exist between the elements present in a chemical compound and that such differences are relatively small in the case of stable forms of combination and relatively great in the case of unstable linkages.[2] For purposes of convenience the existence of a condition of tension within a given molecule may be roughly represented by means of plus and minus signs. These considerations are of increasing importance in interpreting reactions in the field of Organic Chemistry and will, therefore, be developed in some detail in the succeeding chapter.

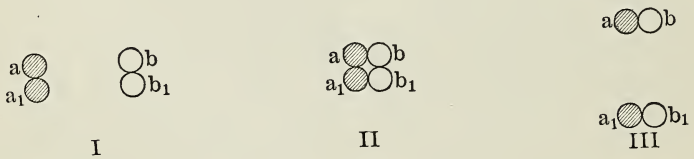
[1] Ber., **52**, 263 (1919).

[2] Ber., **37**, 1646 (1904).

CHAPTER IX

RECENT THEORIES IN REGARD TO THE MECHANISM OF CHEMICAL REACTIONS

The direct union of molecules was recognized very early in the development of chemical theory. To this class of reactions belong not only additions of Cl_2, HCl, etc., to molecules containing doubly bound carbon atoms, but also substitutions of hydrogen by halogen and other acid radicals. Kekulé, in his "Textbook of Organic Chemistry," conceives the matter in the following way: "in any chemical action the two reacting molecules are first drawn together by the mutual exercise of chemical affinity and then ultimately become attached to each other. In this closer association, individual atomic attractions make themselves felt, with the result that atoms which had previously been present in two different molecules come into very close proximity. Such rearrangements may finally lead to the disruption of the whole complex and the formation of entirely new molecules."

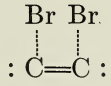


Kekulé's conception of the mechanism of chemical combinations is attracting renewed attention at the present time, because it is needed to explain the formation of intermediate products. In the past only a few addition products of this type were known, largely because they are usually very unstable and are therefore difficult to isolate. Since, however, the existence of such substances has been postulated with increasing frequency in the course of the development of modern theory, methods and reagents [1] have been devised by means of which it is now possible to recognize and also frequently to isolate these products. In addition to the well-known optical methods, methods

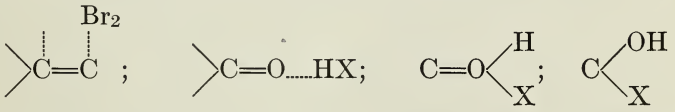
[1] $C(NO_2)_4$, $SnCl_4$, $SnBr_4$, etc., have been used successfully. See Annalen der Chemie, **376**, 286 (1910).

of thermo analysis have been perfected by R. Kremann, Ph. Guye, von Holleman, Schmidtlin and others, so that they can now be applied successfully in the field of organic chemistry. As a result H. Wieland, P. Pfeiffer, G. Reddelien and others have been able to identify a number of intermediate products and to study them much more closely than had previously been possible.

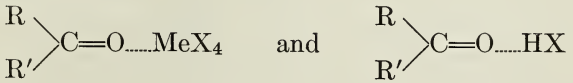
For a long time the constitution of these compounds remained an open question. It was debated as to whether they should be conceived in terms of Thiele's theory, in which case disruption of the bromine molecule, for example, must be supposed to have taken place,



or in terms of simple molecular combinations, in which case the exercise of free affinity may be depicted in any of the following ways:



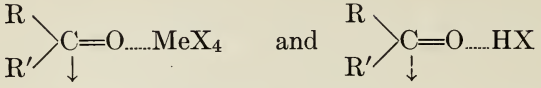
The solution of this problem has finally been arrived at, and a satisfactory picture of the mechanism of addition reactions has been evolved through the efforts of P. Pfeiffer [1] and others co-operating with him. As a result of a very thorough and systematic investigation it has been demonstrated that substances which contain carbonyl—such as aldehydes, ketones, acids, esters, amides, etc.—react with metallic chloride (MeX_4) and with acids (HX) to give addition products which closely resemble each other in composition and in the ease with which they decompose. The general behavior of these substances is most readily explained on the assumption of a similarity in constitution, and it is supposed that the addend (MeX_4 and HX) is first joined to the oxygen of the carbonyl group by means of a small residual valence, viz.,



In the course of time a greater fraction of the total affinity of the oxygen may be exercised in this union, the actual amount varying in different instances and depending, in general, upon the nature of the addendum. In every case it follows, however, that a proportionally great fraction of the total affinity of carbon will be set free, and this

[1] Annalen der Chemie, **376**, 285 (1910); **383**, 92 (1911); **404**, 13 (1914).

is represented graphically by Pfeiffer by means of an arrow directed downward:



Such an increase in the free energy of the carbon atom makes itself manifest in the form of increased chemical reactivity.

By means of this conception it is possible to understand the catalytic action which is so frequently attributed to metallic salts and acids, and to explain many other phenomena in the most diverse fields. It is frequently referred to as " Pfeiffer's Theory of Halochromism " because it was originally advanced to explain the phenomenon of halochromism, and will be referred to later, not only in this connection but also in connection with a discussion of " Walden's rearrangement."

In pursuing the present development, G. Reddelien's [1] investigations must now be considered. These remarkable discoveries are based upon Pfeiffer's theory and are concerned with the addition products which are formed by the action of nitric acid upon carbonyl groups in organic combinations. Many of these compounds have been isolated, but, of the innumerable substances which Reddelien describes, only a few need be referred to for purposes of discussion, viz., $C_6H_5CHO \cdot HNO_3$, $C_6H_5COCH_3 \cdot HNO_3$, $C_6H_5COC_6H_5 \cdot HNO_3$, and $C_{10}H_{16} \cdot HNO_3$ (camphor nitrate). It seems probable that the nitric acid reacts in such cases in the sense indicated by Pfeiffer's formulas.

The application of this reaction has been extended by Reddelien, who has discovered that substances containing such groups as —C=N—, and N=N are also capable of forming well-defined but not very stable addition products with HNO_3. Substances with the grouping C=C, on the other hand, fail to give products which can be isolated, although there are numerous indications of addition reactions even in such cases. In later investigations, and after he had observed that the oxidizing action of HNO_3 and other of its properties seem to interfere with the purification of its addition products, Reddelien substituted picric acid for it. This substance is also a very strong acid and gives addition products with carbonyl, carbimine- and azo-compounds, viz.,

$C_6H_5CHO \cdot HOC_6H_2(NO_2)_3$; $C_6H_5COCH_3 \cdot HOC_6H_2(NO_2)_3$, etc.; $(C_6H_5)_2C{=}N \cdot C_6H_5 \cdot HO\ C_6H_2(NO_2)_3$, (benzophenoneanil picrate) and $C_6H_5N{=}NC_6H_5 \cdot HOC_6H_2(NO_2)_3$, (azobenzene picrate).[2] These com-

[1] Jour. prakt. Chemie, **91**, 213 (1915).

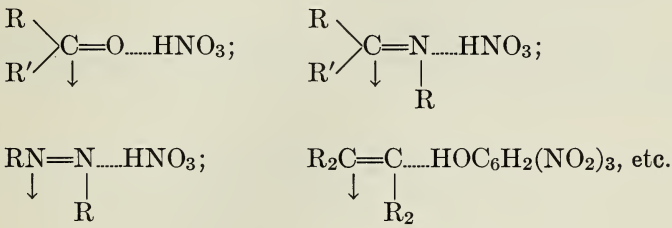
[2] Jour. prakt. Chemie, **91**, 214 (1915).

pounds are assumed to possess constitutional formulas which are analogous to those which have already been assigned to the corresponding nitrates.

Minor differences in properties have been observed in the case of these two classes of addition products. Thus the nitrates are very unstable and, even in the presence of water, are broken down either wholly or partially into their components:

$$C_6H_5CHO \cdot HNO_3 + H_2O \rightarrow C_6H_5CHO + HNO_3 \cdot H_2O$$

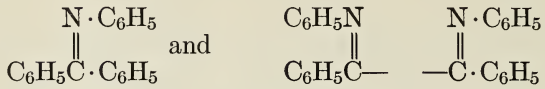
In the preparation of these substances it is, therefore, necessary to maintain a constant concentration of the nitric acid, since a too strong acid tends to nitrate the original material and a too weak acid tends to decompose the product. The picrates behave analogously, but in their case solution tension (i.e., osmotic pressure) is greater than the affinity of the components. If, for example, a given picrate is dissolved in a solvent in which one component is very soluble and the other only slightly soluble, decomposition will take place and will be partial or complete according to the conditions of equilibrium in the system.[1] All such compounds show increased chemical reactivity, which may be accounted for readily in terms of Pfeiffer's theory of halochromism, viz.,



Reddelien made the further discovery that substances which contain conjugate systems of double bonds give addition products which are markedly less stable than those described in the preceding cases. For example, while benzophenone nitrate $(C_6H_5)_2CO \cdot HNO_3$, and fluorenone nitrate $(C_6H_4)_2CO \cdot HNO_3$ are fairly stable and can be kept from one-half to two days, benzil nitrate $(C_6H_5CO)_2HNO_3$, on the other hand, decomposes almost immediately and phenanthraquinone nitrate $(C_6H_4CO)_2 \cdot HNO_3$ breaks down in less than half an hour. The same general relations have been observed to hold

[1] Jour. prakt. Chemie, **91**, 216 (1915); also Behrend, Jour. Physikal. Chemie, **10**, 278 (1892).

in the case of the addition products of benzophenone-anil and benzil-dianil,

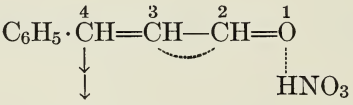


An important exception to this general rule has been observed in connection with substances in which ethylene forms the second group in a conjugate system of double bonds, as for example:

$$O{=}C\cdot C{=}C; \quad N{=}C\cdot C{=}C; \quad C{=}C\cdot C{=}C$$

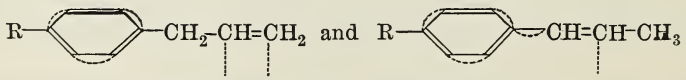
In such cases the stability of the addition product is greatly increased, as is shown by the fact that the nitrate and picrate of cinnamic aldehyde can be kept for weeks, while the corresponding products with benzaldehyde decompose after a few hours. Benzalacetone, benzalacetophenone and dibenzalacetone show the same general relation to acetophenone and benzophenone. By means of these reactions, Reddelien was even able to distinguish numerically between the relative affinity of such groups as $O{=}C\cdot C{=}O$; $O{=}C$; and $O{=}C\cdot C{=}C$. This was accomplished by decomposing the corresponding nitrates with dilute nitric acid and measuring the amount of hydrolysis. Results show this to be 70, 36, and 6 per cent in the case of $C_6H_5CO\cdot COC_6H_5\cdot HNO_3$, $C_6H_5COC_6H_5\cdot HNO_3$, and $C_6H_5CH{=}CHCO\ C_6H_5\cdot HNO_3$ respectively.

The constitution of addition products formed by the action of nitric acid upon substances which contain conjugate systems may be represented as follows:



The above figure shows free affinity on the carbon atom in the 4-position with respect to oxygen of the carbonyl and suggests a condition which is similar to one which has been referred to earlier in this text. It may be recalled that Staudinger and Kon have used an analogous conception in interpreting addition reactions in the case of ketenes.[1]

Quantitative differences in the relative reactivity of such unsaturated systems as



[1] Annalen der Chemie. **356**, 102; also "Die Ketene." p. 108, Stuttgart.

have been observed by both Bruni and Tornani [1] and by Thiele and Henle,[2] who point out that, of the two systems, only the latter gives addition products with picric acid. From this it follows that the free affinity present in a given compound must reach a certain value before combination with picric acid can take place. This minimum has apparently been reached in the case of the latter but not in the case of the former substance. Reddelien applies this general conception to explain the deeply colored picrates of benzene, naphthalene and anthracene, viz.,

.[3]

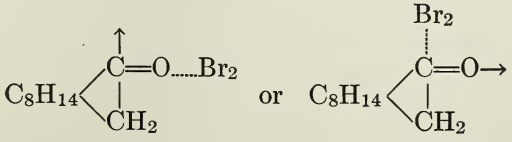
The nitrates differentiate themselves from the corresponding picrates in the tendency which they show to undergo chemical rearrangements. Such transformations result in the formation of nitro compounds and may be supposed to take place according to the following scheme:

$$\begin{matrix} R\cdot CH\rightarrow \\ \| \\ R\cdot CH\ldots\ldots HNO_3 \end{matrix} = \begin{matrix} R\cdot CHOH \\ | \\ R\cdot CHNO_2 \end{matrix} = H_2O + \begin{matrix} R\cdot CH \\ \| \\ R\cdot C\cdot NO_2 \end{matrix}$$

Such a process may be regarded as analogous to the addition of bromine to unsaturated ethylene compounds as formulated by von Reich:[4]

$$\begin{matrix} R\cdot CH \\ \| \\ R\cdot CH \end{matrix} + Br_2 = \begin{matrix} R\cdot CH\rightarrow \\ \| \\ R\cdot CH\ldots\ldots Br_2 \end{matrix} = \begin{matrix} R\cdot CHBr \\ | \\ R\cdot CHBr \end{matrix} = \begin{matrix} R\cdot CH \\ | \\ R'\cdot CBr \end{matrix} + HBr$$

Molecular compounds of the above type are frequently met with and are characterized not only by the fact that they are relatively unstable but also by their tendency to undergo intramolecular rearrangement and so to pass into the corresponding substitution products.[5] Thus, according to Reddelien, dibromcamphor,



[1] Atti. R. Acad. Lincii, 5, 13, II, 184 (1904).
[2] Annalen der Chemie, **347**, 295 (1906).
[3] Compare this formula with that of Pfeiffer, Annalen der Chemie, **404**, 13 (1914).
[4] Jour. prakt. Chemie, **90**, 177 (1914).
[5] Compare H. Wieland, Ber., **40**, 4260 (1907); **43**, 699 (1910).

loses its bromine on standing in the air and passes back into free camphor, but if heated rapidly in a closed tube it loses HBr and is transformed into monobromcamphor. All such molecular compounds may therefore be regarded as representing the primary products which usually form in substitution processes and as the actual forerunners of the final substitution products. They may be formulated in the most general terms by means of the expression

$$\begin{array}{l} A\rightarrow \\ \| \\ A\ldots\ldots M \end{array}$$

where A represents an atom and M, a molecule.

In general it may be said that if the various types of doubly-bound atoms,

$$\underset{\text{I}}{C{=}N}, \qquad \underset{\text{II}}{C{=}O}, \qquad \underset{\text{III}}{N{=}N}, \qquad \underset{\text{IV}}{C{=}C}.$$

are compared, it appears that addition products form most readily in the case of substances which contain I and least readily in the case of substances which contain IV. This order is reversed, however, if the reactivity of the resulting compound is considered. It has been observed for example, that addition products which possess unsaturated ethylene linkages (IV) show the greatest tendency to undergo intramolecular rearrangement and to pass over into the corresponding substitution products.

The rôle which such molecular compounds play in the processes of substitution and orientation will be considered more fully in the next chapter.

CHAPTER X

THE QUESTION AS TO THE CONSTITUTION OF BENZENE

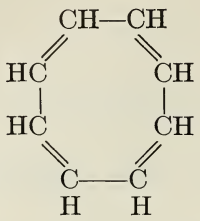
The well-known method for determining crystalline structure which was discovered by M. von Laue and which depends upon the measurement of the interference caused during the passage of Röntgen rays through crystals of various kinds, has been applied recently by P. Debye and P. Scherrer to a study of the behavior of liquid benzene. From the results which have been obtained in this way they have been able to construct a Röntgen diagram and from this to calculate that the space which is occupied by the carbon atoms of the ring (without regard to that required for valence-electrons) is bounded by a circle whose diameter equals 12.4×10^{-8} and has a thickness of at most 1.19×10^{-8} cm. On the basis of these figures it would seem reasonable to conclude that the six carbon atoms of the benzene nucleus probably all lie in a common plane.

This discovery is in general agreement with Kekulé's theory in regard to the constitution of benzene according to which "the six carbon atoms are bound together in a perfectly symmetrical ring structure." This hypothesis was advanced by its author in an effort to give the most comprehensive formulation to the chemical behavior of benzene, but although it has been very generally accepted by chemists it has never been wholly free from certain objections. Even in very early times the non-existence of isomeric *ortho*-disubstitution products made it necessary for Kekulé to add to his original conception the assumptions which are embodied in his "Oscillation Hypothesis"; but, as H. Pauly[1] has again recently pointed out, this explanation was never very satisfactory and has long since been discredited. Even Thiele's partial valency formula in its usual form fails to account for the notable discrepancy between fact and theory which has arisen through the failure in any single instance to isolate isomeric *ortho* derivatives of benzene.

In 1911 the problem involved in the formulation of a satisfactory expression for the constitution of benzene entered a new phase as the

[1] Jour. prakt. Chemie., **98**, 110 (1918).

result of the discovery of cyclo-octatetraene by R. Willstätter and E. Waser.[1] A consideration of the formula of this substance



shows that it differs from the Kekulé formula for benzene only in being composed of 4 instead of 3 conjugate systems of double bonds. This similarity in structure should correspond to a similarity in chemical behavior between the two substances, but as a matter of fact cyclo-octatetraene has all the properties of a decidedly unsaturated compound and in this respect stands in marked contrast to benzene. To quote Willstätter:[2] "cyclo-octatetraene is absolutely different from benzene in its chemical properties. That it must be regarded as a true cyclo-olefine follows from the facts: (1) that it readily adds 4 molecules of hydrogen in the presence of platinum as a catalyst while benzene is entirely unreactive under the same conditions; (2) that it instantly reduces potassium permanganate and adds bromine; (3) that it does not readily form substitution products and does not react with nitric acid to give nitro-derivatives, and (4) that it is unstable and tends to rearrange into more stable isomers."

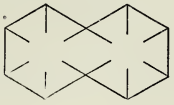
Such marked differences could not be accounted for on the basis of the usual formulas assigned to the substances. It followed, therefore, that in the discussions incident to these discoveries, Claus' formula for benzene and the centric formula of Baeyer and Armstrong again came to the foreground. Both formulas are based upon von Baeyer's conception that the saturation of the six carbon atoms of the benzene ring is of a special kind and peculiar to this particular substance. Claus assumes a diagonal saturation of the six valencies, but this conception cannot be applied satisfactorily without recourse to special hypotheses. As a basis for their theoretical speculations Willstätter and Waser[3] used a modification of the Baeyer-Armstrong centric formula in which the distance of the carbon atoms from the center of the ring is emphasized by means of the following diagram in which

[1] Ber., **44**, 3424 (1911).
[2] Ber., **44**, 3428 (1911).
[3] Ber., **44**, 3430 (1911).

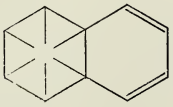
the six valencies of carbon are represented as directed toward a middle point:

The molecular refractions of benzene, cyclo-pentadiene, and cyclo-octatetraene show no important differences and therefore afford no data leading to a solution of the problem presented by the atomic relationships of these substances.

In extending their conception of the benzene ring to naphthalene Willstätter and Waser have discarded Bamberger's centric formula:

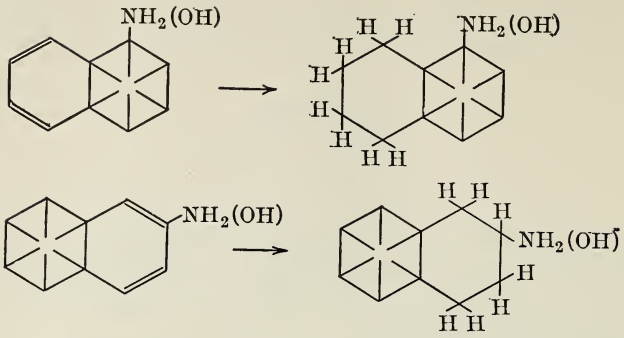


and have substituted in its place:

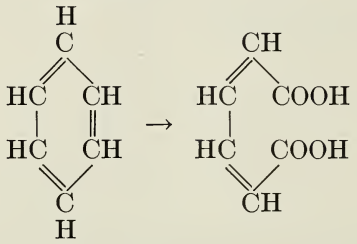


The latter was originally advanced by Harries [1] to explain the action of ozone upon naphthalene, and assumes the presence of only one centric ring, the second ring being represented as olefine in character. This conception affords an analogy to many bicyclic condensation products of the *ortho* diamines and catechols. It also explains the reactivity of carbon in the α-positions. The presence of two different ring structures in the molecule occasions a lack of symmetry, and isomerism, due to substitution in one or the other ring, becomes theoretically possible. While as yet no instances of isomerism of this type have been observed, the question must be raised in the case of each given substitution product of naphthalene as to which of the two possible configurations it represents. Moreover, since α-amino- and hydroxy-naphthalenes behave differently from the corresponding β-derivatives on reduction, the former have come to be commonly regarded as aromatic, and the latter as alicyclic in character. Thus for example:

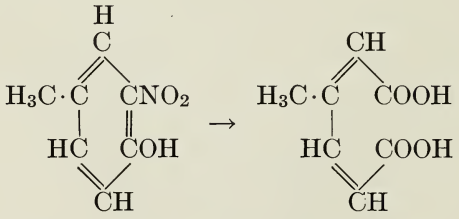
[1] Annalen der Chemie, **343**. 311. 336 (1905).



That the solution offered to the problem of the constitution of benzene by the centric formula is not wholly satisfactory may be seen from the fact that it fails to account for many of the observed properties of the substance. For example H. Pauly [1] has recently pointed out that: (1) benzene passes over into muconic acid during the process of organic oxidation in the organism of a dog or other canines [2]



and: (2) that nitrated *p*-cresol is transformed into β-methyl-muconic acid when oxidized at a temperature of about 100° under the influence of sulphuric acid: [3]



Neither of these reactions can be accounted for on the basis of the centric formula for benzene since on this assumption the ring would

[1] Jour. Prakt. Chemie, **98**, 107 (1918).
[2] Jaffé, Zeitschr. f. physiol. Chemie, **62**, 58 (1909).
[3] Pauly, Gilmour and Will, Annalen der Chemie, **403**, 119 (1914); **416**, 1 (1918).

be expected to open in the following way

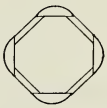
and would result in the formation of butene dicarboxylic acids:

$$\begin{array}{l} CH_2\text{—}C\text{—}COOH \\ \;\;| \qquad\;\; \| \\ CH_2\text{—}C\text{—}COOH \end{array}$$

Substances of this type have never as yet been observed to rearrange to give muconic acids.[1]

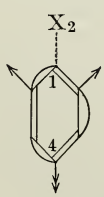
The attention of chemists was again directed to Thiele's formulas for benzene, naphthalene and related compounds when, following the discovery of cyclo-octatetraene, Reddelien[2] took occasion to point out that the observed differences in the chemical properties of this substance and benzene might be accounted for on the basis of Thiele's theory:

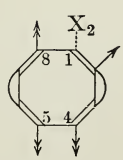
Benzene



Cyclo-octatetraene

For while both unsubstituted compounds may be regarded as representing inactive conjugate ring systems, it does not necessarily follow that a system of three double bonds will be affected in the same way as a system of four double bonds by the action of new atoms or groups. Indeed the differences in the chemical behavior of the two substances show that this is not in fact the case. To explain these differences on the basis of the above formulas Reddelien argues that if the action of a molecule of reagent such as X_2 is regarded as being primarily an addition reaction, it follows according to Thiele's theory that such addition will be followed immediately by a redistribution of affinity, i.e.,



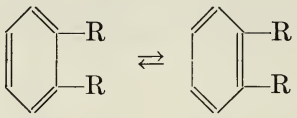


[1] Compare also Jour. prakt. Chemie, **98**, 107 (1918), and Auwers, Annalen der Chemie, **415**, 139 (1917).

[2] Jour. prakt. Chemie, **97**, 225 (1917).

In the case of benzene this will correspond to a tendency on the part of the substance to form *para* derivatives. In the case of cyclo-octatetraene the effect is somewhat more complicated. As the above diagram shows the system of eight atoms has been broken down into two separate conjugated systems, 1–4 and 5–8. The two butadienes which compose these systems may be supposed to act more or less independently if the above diagram is correct and it may, therefore, be said that the affinities of carbon,—which in cyclo-octatetraene are equally distributed and almost wholly neutralized,—have become polar in character. This condition would readily account for the unsaturated character of such a compound and also for its tendency to form bridge compounds (1–4 or 8–5).

Thiele's formula for benzene is of course open to the same objection as Kekulé's formula in that it presupposes the existence of isomeric derivatives of the type:



While no such compounds have as yet been isolated Reddelien is of the opinion that the existence of such isomers is possible. They are obviously by their very nature extremely sensitive substances, but the development of a more delicate technique may, he thinks, in time lead to their discovery. Until, however, new methods have been developed and either positive or negative results obtained, the non-occurrence of these isomers offers no really convincing evidence against the Kekulé-Thiele expression for the constitution of benzene.

A further objection to the Kekulé-Thiele formula for benzene has been urged on the ground that it presupposes the presence of three pairs of ethylene linkages while as a matter of fact all aromatic compounds behave more or less like saturated substances. Reddelien [1] meets this objection by means of the following argument: the fact that a given compound reacts readily in the presence of a given reagent may be construed to mean either one of two things: (1) that the reaction proceeds rapidly, (2) that the yield is good. In the second case it must be assumed that the conditions of equilibrium are such as to favor the formation of the particular reaction-product. It is obvious that the rate of reaction in itself affords no measure of affinity because catalysts and anticatalysts have the power either to hasten or to retard chemical action enormously. A direct measure of

[1] Jour. prakt. Chemie, **91**, 225 (1915).

affinity is possible only when the conditions of equilibrium favor the formation of the reaction-product. The relation between the rate of reaction and affinity is expressed by the equation:

$$\text{Rate of Reaction} = \frac{\text{Affinity}}{\text{Chemical Resistance}}$$

in which chemical resistance represents a very imperfectly known quantity. Obviously a direct relation between rate of reaction and affinity can be established only in cases where the chemical resistance is approximately the same under the same conditions.

Reasoning along these lines Reddelien comes to the conclusion that since the slowness with which a given reaction proceeds is not a measure of affinity, the presence of three pairs of double bonds in benzene is shown by the simple fact that benzene reacts with halogen, hydrogen, ozone, etc. The question as to whether the retarding action of catalysts is responsible for the slowness with which benzene reacts,—and if so to what extent,—was then investigated by Reddelien.

An observation made by Luther and Goldberg serves to illuminate this whole problem. These investigators discovered that in the sunlight benzene possesses the power to combine instantly with six bromine or chlorine atoms provided that no oxygen is present during the process. It follows that the oxygen of the air has a retarding effect upon this reaction, or in other words, that it acts as an anti-catalyst. Under these circumstances the rate of reaction obviously affords no measure of the affinity of the reacting molecules. The observed difference in the rate with which additions take place in the case of benzene and its derivatives as compared with unsaturated aliphatic compounds, indicates a difference merely in degree. That it is not a difference in kind is supported by the fact that in certain types of aliphatic compounds the ethylene linkage is just as unreactive as in benzene [1] and that every variation between this and very reactive ethylene derivatives has been observed. The presence of ethylene linkages is not proved or disproved merely by the behavior of the substance in the presence of halogen.

Benzene as compared with unsaturated aliphatic compounds is oxidized very slowly by permanganate solution. This again may be regarded as a difference in degree rather than in kind. In this case the oxides of manganese probably act as anticatalysts since it has been observed that the oxidation of cyclohexane may be greatly accelerated by working in acid solution.[2] Moreover benzene reacts with ozone to

[1] Bauer, Jour. prakt. Chemie, **72**, 201 (1905).

[2] Wieland, Ber., **45**, 2616 (1912).

give a triozonide, and if as Harries [1] believes ozone is a typical reagent for detecting the presence of ethylene linkages the existence of three such linkages in benzene is demonstrated.

It has frequently been observed that benzene does not add hydrogen to any appreciable extent under the catalytic influence of Ni, Pt, and Pd, and that it therefore differs from unsaturated compounds of the aliphatic series which under the same conditions are readily reduced. Recently, however, it has been discovered that this difference in the behavior of benzene is due to the presence of small quantities of thiophene which acts as an anticatalyst, and that when absolutely pure benzene is treated with hydrogen under the above conditions it is reduced instantly and completely.[2]

A consideration of the above facts leads to the conclusion that the behavior of benzene is not on the whole so exceptional as has previously been supposed. For while benzene does not show the characteristics which might be expected of a substance possessing three pairs of double bonds, neither do certain aliphatic compounds which undoubtedly possess ethylene linkages. Reddelien, therefore, is of the opinion that Thiele's formula may be accepted for the present as offering the best expression of the constitution of benzene since it affords an exceptionally satisfactory explanation of the heat relationships and also of the reduction products.

The question as to whether addition-reactions and substitution-reactions represent separate and distinct types, or whether so-called substitution processes may not always be regarded as due to secondary rearrangements following the primary addition of two molecules,— has long occupied the attention of chemists. An important experimental contribution to the solution of this general problem has recently been brought forward by H. Wieland [3] and since it has a direct bearing upon the question of the constitution of benzene it may be considered briefly in this connection. Wieland in co-operation with E. Sakellarios undertook an investigation in regard to the action of nitric acid upon substances which contained unsaturated ethylene linkages. In the case of ethylene itself it was assumed that β-nitroethyl alcohol would form as a primary product by direct addition:

$$CH_2{=}CH_2{+}HO{\cdot}NO_2 \rightarrow NO_2{\cdot}CH_2{\cdot}CH_2OH$$

As a matter of fact the corresponding nitrate, $NO_2{\cdot}CH_2CH_2O{\cdot}NO_2$, was isolated along with glycoldinitrate, $NO_2O{\cdot}CH_2CH_2ONO_2$, by

[1] Harries, Annalen der Chemie., **343**, 335 (1905).

[2] Compt. rend., **132**, 211 (1901); Willstätter and Hatt, Ber., **45**, 1471 (1912).

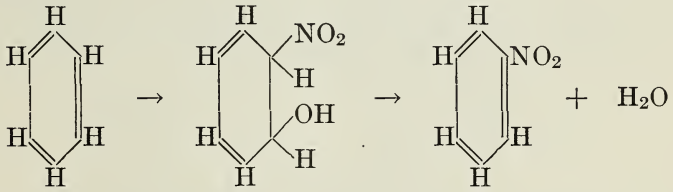
[3] Ber., **53**, 201 (1920).

both investigators. The first of these substances obviously forms as a result of the continued action of nitric acid upon β-nitroethyl-alcohol, which may thus be assumed to represent the primary product of the reaction. The important observation was then made that both β-nitroethylalcohol and the corresponding nitrate may be transformed into nitroethylene,[1]

$$CH_2{=}CH\cdot NO_2$$

by treatment with a dehydrating agent such as phosphorus pentoxide or sodium bisulphate. It would, therefore, seem to follow that this reaction may be added to the list of those which support the view that the mechanism of nitration consists primarily in addition reactions.

In the case of benzene and its derivatives the application of this conception involves the assumption that all nitro compounds represent secondary products. Thus in nitration, a molecule of nitric acid may be supposed to add to the partial valencies which are present on two ethylene carbon atoms and this action is then followed by the loss of one molecule of water:



The whole question of substitution reactions has recently been further illuminated by the discoveries made by H. Wieland[2] in connection with a systematic investigation of the chemistry of the hydrazines. Wieland found that tetrarylhydrazines, as for example $(p\text{-}CH_3\cdot C_6H_4)_2N\cdot N(C_6H_4\cdot CH_3\text{-}p)_2$, and also secondary and tertiary amines, such as $(CH_3OC_6H_4)_2NH$ and $(p\text{-}CH_3C_6H_4)_3N$, give deeply colored addition-products in the presence of acids, halogens, and metallic chlorides. In some cases these addition-products have been isolated, as for example,

$$((CH_3\cdot C_6H_4)_2N\cdot N(C_6H_4CH_3)_2)Br_3;\quad (CH_3OC_6H_4)_3NBr_3$$

[1] Ber., **52**, 898 (1919).

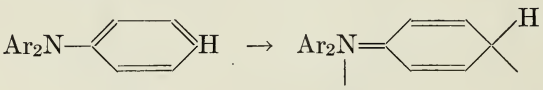
[2] "Die Hydrazine," Enke, Stuttgart, 1913, p. 69; Ber., **40**, 4260 (1907); **43**, 699 (1910).

All decompose more or less readily and in so doing yield substitution products of benzene:

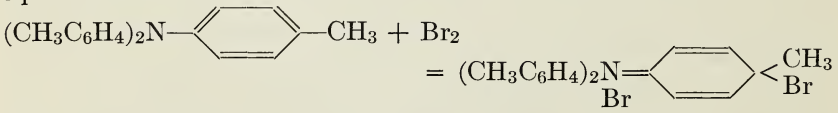
$$2(p\text{-}CH_3\cdot C_6H_4)_3NBr_3 \rightarrow (CH_3(Br)C_6H_3)_3N + (CH_3C_6H_4)_3N,$$

$$2(CH_3OC_6H_4)_2NHBr_2 \rightarrow (CH_3O(Br)C_6H_3)_2NH + (CH_3OC_6H_4)_2NH\cdot HBr$$

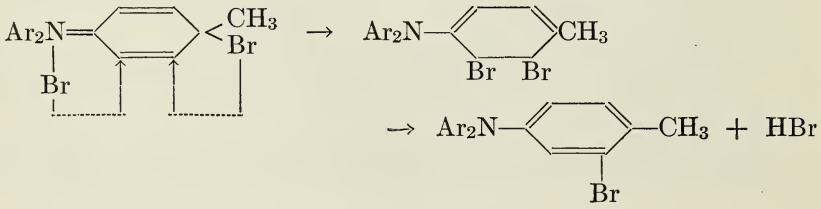
Wieland is of the opinion that these colored addition-products represent primary products in all reactions involving substitutions in the benzene ring and that they play an important rôle in all such processes. In the particular instances which have just been cited his interpretation of the mechanism of the transformation is as follows: in the case of primary and secondary amines addition takes place on the nitrogen atoms and is due to the relatively large fraction of free affinity possessed by these atoms. In the case of tertiary amines and tertiary hydrazines there is relatively less free affinity, as is shown by the fact that the nitrogen is unable to pass into the pentavalent condition with the accompanying normal salt formation, and under such circumstances the processes of halogenation, nitration, and sulphonation cannot be assumed to take place as the result of direct additions. On the other hand, intramolecular rearrangements of tertiary aromatic hydrazines and amines may lead to the reappearance of active nitrogen in the molecule, viz.,



In this way reactions involving direct additions would again become possible, and in the case of bromine could be represented by the equation:



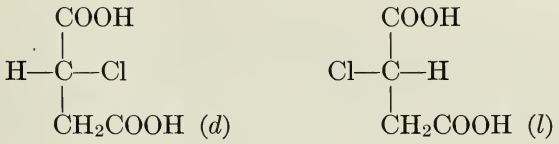
This interpretation readily accounts for the color of the resulting quinoidal product. Subsequent rearrangement takes place in the sense



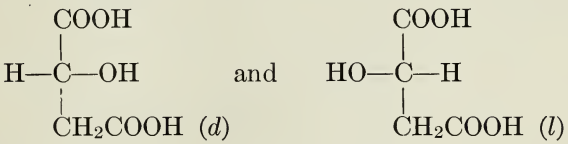
Wieland assumes that similar interpretations may be applied in the case of all substitutions in the benzene ring.

Emil Fischer offers an explanation of the mechanism of substitution which is essentially different from that of Wieland although it, too, rests upon the assumption of the formation of intermediate products. In order to understand it, it will first be necessary to consider the so-called Walden Rearrangement.[1]

Chlorosuccinic acid and other similar compounds contain an asymmetric carbon atom and therefore exist in *dextro, laevo* and *racemic* modifications. The difference between the *dextro* and *laevo* acids may be shown by means of a diagram in which atoms are represented as occupying positions in the same plane:



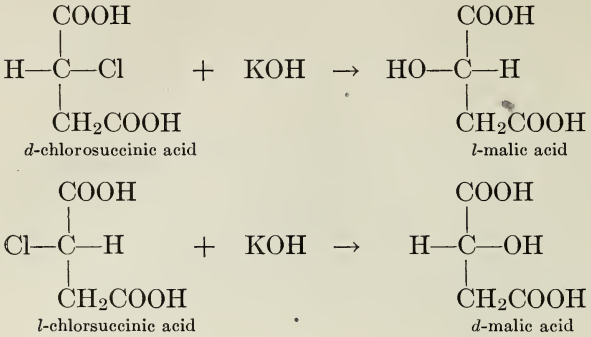
Bases such as AgOH, KOH and NH_4OH react with these substances to give *d*- and *l*-malic acids and metallic chlorides. In terms of the generally accepted conception of substitution the halogen in these compounds has been replaced by hydroxyl giving:



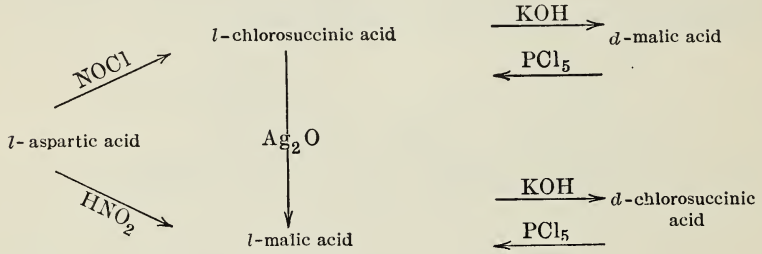
In these transformations no change of polarity sign is brought about by the action of silver hydroxide; *d*-chlorosuccinic and *l*-chlorosuccinnic acids giving *d*- and *l*-malic acids respectively. On the other hand, when stronger alkalis like KOH and NN_4OH are used deep-seated intramolecular changes result in such cases. Walden discovered that the transformation involved a change from *dextro*-chlorosuccinic acid to *laevo*-malic acid, and from *laevo*-chlorosuccinic acid to *dextro*-malic acid. It was, moreover, possible to follow the course of this reaction directly by means of a polariscope and to observe a gradual change in the optical rotation of the mixture from right to

[1] Ber., **29**, 133 (1896); **30**, 2795, 3146 (1897); **32**, 1833, 1855 (1899); also compare P. Walden, "Optische Umkehrerscheinungen," F. Vieweg und Sohn, Braunschweig, 1919.

zero to left. Thus in a very mild chemical reaction a change of place is affected by atoms in union with the asymmetric carbon atom:



Many other instances of a change in the nature of the rotation of optically active substances have been observed in connection with similar reactions and the process has come to be known as the Walden rearrangement in honor of its discoverer, P. Walden.[1] The following scheme, taken from Walden's memoir,[2] shows the cycle of changes possible with cholorosuccinic and malic acids, whereby the sign of rotation may be changed at will:



Many new and interesting examples of rearrangements of this type have been investigated by Emil Fischer[3] and are regarded by him as throwing new light upon the mechanism of substitution. Up to this time the Walden rearrangement had been considered abnormal. Since, however, it was observed so frequently and took place so regularly, Fischer concluded that it must represent a normal rather than an abnormal process and that, therefore, this type of reaction ought not to be

[1] Loc. cit.

[2] See Annual Reports of the Chemical Society (1911), 60; The British Assoc. Report (1912), 687, by McKenzie; Presidential Address to the Cnemical Society by Frankland, Jour. Chem. Soc. **103,** 717 (1913).

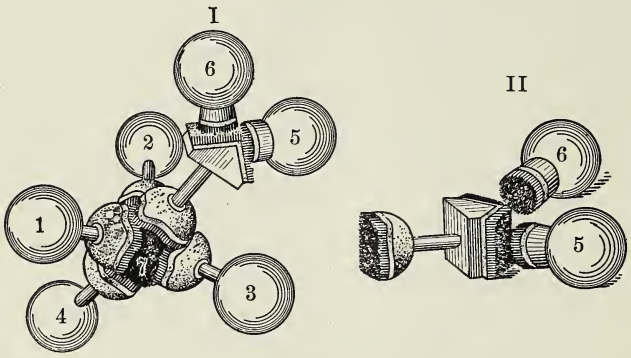
[3] Ber., **40**, 489, 1051 (1907); **41**, 889, 2891 (1908); **42**, 1219 (1909); 43, 2020 (1910); Annalen der Chemie, **381**, 123 (1911); **386**, 374 (1912).

considered as an exception but as representing a very general phenomenon. If this is true it follows that previous views in regard to the process of substitution must be false. If the OH group actually takes the place of the halogen in the case just cited, it is difficult to understand why it does not keep this position instead of changing it with such frequency and regularity. To correctly interpret this phenomenon it is necessary to suppose that in substitution reactions the entering group does not actually take the place of the group which is replaced, but that it may assume quite as readily some other position with reference to the carbon atom. Such an explanation is obviously impossible in terms of rigid stereochemical conceptions and Emil Fischer, therefore, formulated it in terms of Werner's theory.

Fischer assumes that the affinity of a free atom is not *a priori* divided into separate units (valencies), but that it operates as an attractive force which radiates equally in all directions from the center of the atom. When other atoms combine with carbon they seek to dispose themselves in such a way with reference to the circumference of the carbon atom as to occasion the greatest possible saturation of their respective affinities. Thus a perfectly definite fraction of the total affinity of the carbon atom is exercised in holding each of the several atoms in union with it, the amount varying according to the nature of the combining atom. In this way the total affinity of the atoms is not exhausted and residues of free affinity may be imagined as almost always present on the individual atom. The existence of such free affinity accounts for the formation of so-called molecular compounds by the interaction of substances which are apparently already fully saturated. Kekulé's assumption that all chemical reactions are primarily addition-reactions which are followed by secondary rearrangements has thus been applied by Fischer to cases of substitution. He supposes that one group does not directly replace another but that every type of reaction is preceded by the formation of an addition-product, and that in the course of the subsequent decomposition of this primary product new arrangements of the substituents with reference to the carbon atom become possible. Accordingly the new group may either occupy the same position as that of the atom or group which it replaces, or it may assume a different position. If the latter happens in the case of an asymmetric carbon atom the result will be a Walden rearrangement. If both types of reaction take place, racemic mixtures will result in which racemization may be partial or complete depending upon the chemical nature of the substituents in the molecule.

In order to visualize clearly this process Fischer made use of the

following model: the central carbon atom is represented by a small wooden sphere, the surface of which is covered with wire brush. Colored celluloid balls are used to represent the substituent atoms, and are fastened by means of small wooden pegs to flat pieces of cork. The under surfaces of the cork are also covered with wire brush, thus making possible a junction between the various substituents and the carbon atom at any point on the surface of the latter. Fig. I shows a central atom, 7, which is holding the four substituents, 1, 2, 3 and 4, and which in addition is holding a system compounded of two separate units 5 and 6. The parts of this system are represented separately in Fig. II, which shows two balls 5 and 6, similar in construction to 1, 2, 3 and 4, and the mechanism by which their joint union with the central atom is effected.



This model serves to demonstrate the formation of addition-products as preliminary to all processes of substitution. Thus, for example, in the addition of ammonia to α-brompropionic acid, the balls 1, 2, 3 and 4 represent respectively H, Br, CH_3, and $COONH_4$, while 5 and 6 represent H and NH_2, the latter being secured by means of a partial valency to the central carbon atom. This compound subsequently breaks down with loss of HBr. The position left vacant by the bromine may then be filled by NH_2 or by any one of the three remaining substituents, supposing that these are free to move. In the latter case NH_2 would come to occupy a position different from that previously held by bromine and a Walden rearrangement would have occurred. In cases where both processes take place side by side partial or complete racemization results.

While this conception in regard to the mechanism of substitution reactions has been developed in connection with the study of substances which possess an asymmetric carbon atom, it may be extended

to include all known cases of substitution and the perfectly general assumption may then be made that in the case of so-called substitution processes the entering group need not necessarily take the place of the group which it eventually comes to replace, since a variety of other positions are equally well open to it.

As Fischer points out the same general conception may also be applied to the transformation of an unsaturated into a saturated compound. It has been observed, for example, that when bromine adds to fumaric acid changes in the configuration of the molecule may occur.[1] As in the case of the preceding illustrations such changes may be readily followed because the resulting compound contains an asymmetric carbon atom. They are, however, in no sense to be regarded as due to the special action of the halogen but are of a perfectly general and normal character.

In the course of the development of his theory of valency, and almost simultaneously with Fischer, Werner evolved a similar conception in regard to the process of substitution.[2] As a result of exhaustive investigations in regard to the configuration of stereoisomeric cobalt compounds, Werner found that changes similar in nature to the Walden rearrangement frequently occur in the course of substitution, addition, and displacement reactions and that in such cases the new groups entering into the complex radical do not assume the same relative position in space as was occupied by the atoms or groups which they replace. It has been suggested that such processes are similar to the rearrangements of labile into stable forms of the case of stereoisomers, but this is not in actual harmony with all of the facts.

In order to understand Werner's explanation of the problem certain facts must be borne in mind: (1) spacial considerations necessarily limit the number of atoms which may actually be imagined as in direct union with a central atom, and the number of such atoms must be regarded as comparatively small; (2) the space which they occupy is spoken of as the first sphere of the central atom, but atoms in this sphere may in turn be bound to other atoms, which latter may be located in a second sphere with reference to the central atom; (3) the term "coordination number" is used to describe the number of atoms which form the first sphere. (In the case of carbon this number is four.)

[1] Annalen der Chemie, **381**, 123 (1911); **386**, 376 (1912); also compare Michael Jour. prakt. Chemie, **38**, 6 (1888); **40**, 29 (1889); **43**, 587 (1891); **46**, 209, 381 (1892), **52**, 289 (1895); **75**, 105 (1907).

[2] Ber., **44**, 873 (1911).

The following rules have been deduced from a study of stereoisomeric compounds of cobalt:

1. The central atom of the complex radical exercises an attractive power over groups which are found outside the first sphere, and tends to draw these groups into the space limits of the first sphere.
2. The strength of this attraction depends upon the chemical nature of these groups.
3. The position in the first sphere which an entering group may occupy is conditioned by the *direction* of the force acting between it and the central atom.
4. Entrance into a coordinately saturated compound can take place only as the result of a loss of some atom or group already present. It follows naturally that the group which is least firmly bound will be most readily displaced, and that this will in no way depend upon the location of such a group with relation to the position occupied by the entering group.

Werner made furthermore the discovery that intermediate addition-products (AX·BY) are frequently formed during the course of a substitution reaction of the type:

$$AX + BY \rightarrow AY + BX$$

Such additive-compounds are sometimes quite stable, but when decomposed they yield the products represented in the above equation.

In brief Werner supposes that substitution processes take place in three phases:

1. The formation of addition-products in which the groups that are finally split off become slightly detached from the atoms to which they are bound.[1]
2. The penetration of the first sphere by atoms or groups which are drawn away from their original positions in the second sphere by the attractive force of the central atom.
3. The displacement of an atom or group coordinately bound in the first sphere as the result of a weakening of the attraction by which it is bound to the central atom.

Although these conceptions were developed from experimental data in the field of inorganic chemistry, they have also been applied

[1] Compare, W. Manchot, Annalen der Chemie, **387**, 257 (1912).

by Werner to organic compounds. Thus the substitution of hydroxyl by halogen, represented by the equation:

$$R_3COH + H \cdot Hal. \rightarrow R_3C \cdot Hal. + H_2O$$

may be regarded as taking place in the following stages:

$$R_3COH + H \cdot Hal. \rightarrow (R_3COH_2)Hal.$$

$$(R_3COH_2)\,Hal. \rightarrow R_3C \cdot Hal. + H_2O$$

The position which the entering atom or group will occupy in the molecule does not depend upon that of the substituted group but upon the direction of the attractive force emanating from the central atom. It follows that under favorable circumstances asymmetric compounds which are dextro rotatory may give derivatives which are laevo rotatory and vice versa. In short on the basis of these observations as well as of those brought forward by Fischer, Walden rearrangements may be regarded as phenomena which are normal rather than abnormal in character.[1]

In all discussions of substitution in the benzene ring it is generally assumed that the six hydrogen atoms of benzene are equivalent. On this assumption it follows that in the reaction between benzene and nitric acid, each of the six hydrogen atoms may be replaced under the same conditions with equal ease by a nitro group to give nitrobenzene. The situation is quite different, however, as soon as the substitution of one hydrogen atom has taken place since the remaining five hydrogen atoms are no longer equivalent, and as is well known three isomeric products result from the replacement of a second hydrogen atom in a mono-substituted benzene derivative. These substances are usually formed not in the same but in different amounts and this is explained as due to the fact that the speeds of reaction are different in the case of the *ortho*, *meta*, and *para* isomers respectively. In other words, certain of the five hydrogen atoms in a mono-substituted benzene are more reactive than others and the three isomers are formed in different proportions depending upon the character of the mono-substituted compound.

It has been observed, for example, that the substituted group in mono-substitution products of benzene exercises a directive or orientating influence upon a second entering group, so that in certain instances *ortho* and *para*, and in other instances *meta* derivatives

[1] Compare Pfeiffer, Annalen der Chemie, **383**, 123 (1911).

result. Even in 1875, Hübner [1] and a year later, Nölting [2] were able to enumerate specific groups which were capable of directing substitution in a given manner. For example, strongly negative groups such as NO_2, SO_3H, COOH and others were known to induce substitution in the *meta* position while positive, neutral, or weakly acid groups, such as NH_2, CH_3, OH, Cl, Br, etc., favored substitution in the *ortho* and *para* positions. According to Nölting the halogens belong to the class of weakly acid groups. Many reactions of this type have been studied by Brown and Gibson,[3] by Armstrong [4] and also by Vorländer [5] and a number of rules have been formulated in regard to them. According to Vorländer, for example, *meta* substitution products are formed in cases where the element of the entering group is unsaturated, while *ortha* and *para* derivatives are formed in cases where the element is saturated. These rules, however, suffer too many exceptions to be classed as laws.

In general, it may be said that the presence of NO_2, SO_3H, or COOH favors the formation of *meta* substitution products. This is also true of CHO, $COCH_3$ and CN although here relatively few cases of substitution have been systematically studied. All other groups have a more or less pronounced influence in the direction of *ortho* and *para* substitution. In every case one isomer generally forms the main product of the reaction, a second is present in smaller but still considerable quantities, while the third is either completely absent or present in such small quantities as to be negligible. Thus in the case of substitution in the *meta* position, for example, there is always formed simultaneously a mixture of *ortho* and *para* derivatives, but in this mixture either the *ortho* or the *para* derivative predominates while the other is negligible. In the case of *ortho* and *para* substitution, a mixture results in which the *para* derivative usually predominates and which contains none or almost none of the *meta* compound.

These rules hold under normal conditions but several exceptions have been observed. Thus aniline usually reacts with nitric acid to give a mixture of *ortho* and *para* nitroaniline. If, however, nitric acid is added to aniline which has been strongly acidified with sulphuric acid, *meta* nitroaniline is formed. In the substitution of halogens, catalytic agents such as the metallic halides, iodine, etc.,

[1] Ber., **8**, 873 (1875).
[2] Ber., **9**, 1797 (1876).
[3] Jour. Chem. Soc., **61**, 367 (1892).
[4] Ibid.
[5] Annalen der Chemie, **320**, 122, (1902).

have been observed to exercise a directive influence upon the position of the entering atom or group.[1]

It has been generally supposed that the process of substitution in the benzene ring consists simply in the direct replacement of hydrogen by some other atom or group. Thus, for example,

$$C_6H_5NH_2 + HO\cdot SO_2OH \rightarrow NH_2\cdot C_6H_4\cdot SO_2OH + H_2O$$

Any one who has prepared sulphanilic acid knows, however, that the primary product of the reaction between aniline and sulphuric acid is aniline sulphate, which forms as a precipitate and which passes over into sulphanilic acid only upon heating. Thus the primary action of the acid does not involve the benzene ring as might naturally be supposed, but the primary amino group in the side chain. Bamberger[2] has also demonstrated experimentally that sulphonic acids may be formed from sulphates of aniline, having actually succeeded in preparing phenyl sulphamic acid, $C_6H_5NH\cdot SO_2OH$, from aniline sulphate by elimination of water. This compound is very unstable in the presence of free acids. With dilute acids it rearranges to give aniline-*o*-sulphonic acid, and with concentrated acids at high temperatures, sulphanilic acid:

$$C_6H_5\cdot NH_2\cdot HOSO_2OH \rightarrow C_6H_5\cdot NH\cdot SO_2OH$$

$$\rightarrow C_6H_4(NH_2)(SO_3H(o\text{-})) \rightarrow C_6H_4(NH_2)(SO_3H(p\text{-}))$$

From this it follows that in the sulphonation of aniline the replacement of hydrogen in the benzene nucleus is not direct, but indirect. Nitration of aniline might naturally be assumed to take place in the same way:

$$C_6H_5\cdot NH_2\cdot HONO_2 \rightarrow C_6H_5\cdot NH\cdot NO_2$$

Aniline nitrate — Phenylnitramine

$$\rightarrow C_6H_4(NH_2)(NO_2(o\text{-})) \rightarrow C_6H_4(NH_2)(NO_2(p\text{-}))$$

o-Nitraniline — *p*-Nitraniline

Experimental evidence in support of this has, indeed, been offered by Bamberger[3] who has obtained the same mixture of *ortho* and *para* nitraniline from phenylnitramine as is obtained by nitrating aniline.

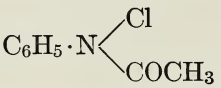
[1] Holleman, "Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910, Veit and Co.

[2] Ber., **26**, 490 (1893); **27**, 361 (1894); **28**, 401 (1895); **30**, 654, 1261 and 2274 (1897).

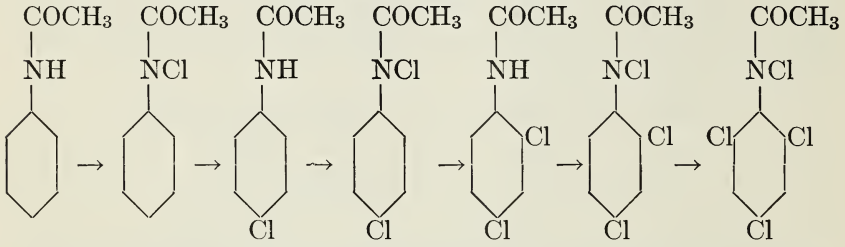
[3] Ber., **30**, 1252 (1897); Störmer, Ber., **31**, 2528 (1898).

Such a conclusion is, nevertheless, disputed by Holleman,[1] who definitely maintains that rearrangement of *ortho-* into *para*-nitraniline does not take place in this case, and that the relations must be regarded as much more complicated.

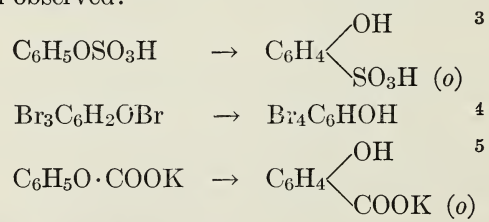
In general, the chemical nature of the substituent in the side chain seems to determine whether a second substituent will assume an *ortho* or a *para* position in the benzene ring. Chattaway and Orton [2] have found, for example, that N-chloracetanilide,



rearranges to give *p*-chloracetanilide, $Cl \cdot C_6H_4 \cdot NH \cdot COCH_3$, and does not form the corresponding *ortho* derivative. If, however, the hydrogen in the *para* position is substituted by another group rearrangement results in the formation of a derivative of *ortho*-chloracetanilide. The complete chlorination of the anilide may therefore be assumed to take place according to the scheme:



Other cases of indirect substitution will be considered in a later chapter dealing with the subject of intramolecular rearrangements. It may be added, however, that there are certain indications of indirect substitution of phenol hydrogen since the following rearrangements have been observed:



[1] Ber., **44**, 704 and following (1911).

[2] Ber., **32**, 3573, 3635 (1899); Blanksma, Rec. trav. chim. des Pays-Bas, **21**, 327 (1902); Hantzsch, Ber., **33**, 505 (1900).

[3] Ber., **9**, 55, 1715 (1876); **11**, 1907, (1878).

[4] Annalen der Chemie, **199**, 127 (1879).

[5] Jour. prakt. Chemie, **31**, 407 (1885).

A consideration of the phenomena which have just been described suggests the possibility that substitutions in the *ortho* and *para* positions are always due to molecular rearrangements from the side chain, and therefore always take place indirectly. According to Holleman and Euwes,[1] however, such an assumption is not justified by the facts. Thus, since benzyl bromide does not rearrange to give *o*- and *p*-bromtoluenes under conditions favorable for the formation of these substances, it seems probable that they form as a result of direct substitution. Many other instances of what seems to be direct substitution in the benzene ring are known. Moreover, while *o*- and *p*-substitutions may be direct or indirect depending upon a variety of conditions, very few cases of indirect substitution in the *meta* position have as yet been observed.[2]

A great many attempts have been made to interpret the mechanism of substitution reactions. Certain of these have already been referred to but none have been found which are satisfactory in all respects. Quite recently B. Flürscheim[3] has applied Werner's theory to the phenomena of substitution in an effort to explain the various empirical rules which have been formulated. His views have been developed in part under the influence of Knoevenagel and may be considered briefly at this point.

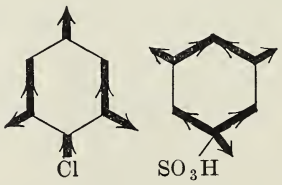
It will be recalled that according to Werner's conception all atoms are assumed to possess a definite amount of chemical affinity which is the same for atoms of the same kind, but different for different kinds of atoms and which radiates from the center of the atom uniformly in all directions. Contrary to the old ideas of valency this attractive force is not imagined as broken up into individual units having constant strength and definite direction in space. Thus when two or more atoms combine they may be supposed to form addition-products of the type suggested by Kekulé. Subsequent adjustments in the relative distribution of affinity among the constituent atoms will depend upon their mutual attractions and also upon their spacial relationships and may lead ultimately to the formation of new compounds. If, for example, a given atom exercises a large part of its total affinity toward a second atom, or in other words is in close combination with this atom, it follows that it has correspondingly less affinity available for holding other atoms which may be in union with it, and these being less firmly bound are capable of rearrangements within the molecule or even of being completely split off from the molecule.

[1] Rec. trav. chim. des Pays-Bas, **27**, 443 (1908).

[2] Jour. prakt. Chemie, **82**, 470 (1910).

[3] Jour. prakt. Chemie, **66**, 321 (1902); **71**, 497 (1905); Ber., **39**, 2015 (1906).

If the six carbon atoms in benzene are symmetrically arranged with reference to each other and to the six hydrogen atoms in union with them, it follows that the distribution of affinity may be supposed to be alike for all. If now one of the hydrogen atoms is replaced by halogen and if it is assumed that the latter atom is more closely bound to carbon than is the former, it follows according to Flürscheim that readjustments in the partition of affinity among the six carbon atoms of the ring must take place. For example, if one carbon atom is exercising a relatively great fraction of its total affinity in holding bromine it must have a relatively small fraction of affinity available for holding the two adjoining carbon atoms. Atoms in the *ortho* position must therefore possess a relatively greater amount of free affinity than before substitution took place. This may in part be used up in holding the two carbon atoms in the *meta* position so that these in turn have less affinity available for holding the carbon atom in the *para* position. In brief, if these assumptions are correct, substitution will result in an increase in the free affinity of those carbon atoms of the benzene ring which occupy *ortho* and *para* positions respectively with reference to the substituting atom or group. Such positions offer therefore points of attack for new substituents. These conclusions are limited, of course, to cases where the entering atom or group is more closely linked to carbon than was the hydrogen which it replaces. In cases where the reverse is true and the substituent is less firmly bound to carbon than was the hydrogen, this carbon atom will exercise a relatively greater attraction for the adjacent atoms. Thus the free affinity of carbon atoms in the *ortho* positions will decrease while that of the *meta* carbon atoms will simultaneously increase. The latter, therefore, become the points of attack for new substituents and *meta* disubstitution products result. For example, if it is assumed that such groups as SO_3H, COOH, NO_2 are less firmly bound to carbon than is the hydrogen which they replace, it is easy to understand in terms of Flürscheim's hypothesis why these groups induce substitution in the *meta* positions. The relationships may be represented diagrammatically as follows:



I II

Heavy lines are here used to denote relatively strong bonds and light lines loose bonds, while the arrows serve to show the position and direction of the affinity which may be neutralized by substituents.

J. Obermiller [1] and Holleman [2] raised objections to this attempt to explain the phenomena of substitution on the following grounds: in the first place there is at present no accurate means for determining whether a given constituent is closely or loosely bound to the carbon atom of the ring. One and the same substituent may appear at one time to be in close combination and at another time in loose combination with carbon. In other words, one and the same compound behaves differently in the presence of different reagents. For example, it may be assumed on the one hand that halogen is closely bound to carbon in monobrombenzene since it does not react readily with KCN, AgOH, KSH, etc., but on the other hand it may equally well be assumed that it is loosely bound since it reacts as readily as alkyl halogen with magnesium in ether solution. "Close combination" and "loose combination" are thus found to be in no sense absolute terms but to need very close definition in every case.

Flürscheim assumes, moreover, that chemical affinity is of the nature of gravitation and this is not in accord with the facts. According to the established laws governing attraction between masses, for example, the force which two bodies exercise toward each other is independent of the presence of a third, and if the earth had two moons instead of one, each would be attracted by the earth just as strongly as if but one were present. On the other hand all observations at the present time seem to show that chemical affinity is much more closely comparable to electricity than to gravitation, and while these relationships do not lend themselves to any simple summary it may still be said that relatively little affinity remains if much is used up.

Even the diagrams suggested by Flürscheim are misleading, according to Holleman, since a heavy and a light line intersect in both *ortho* and *meta* positions, thus apparently indicating the same distribution of affinity in the two cases. It follows, that compounds representing both types (I and II) should give either *para* derivatives as principal products along with a mixture of almost equal quantities of *ortho* and *meta*, or else they should give almost equal quantities of *ortho* and *meta* derivatives. Both of these deductions are contrary to the facts of experiment.

While Flürscheim assumes that substitution is always primarily

[1] Jour. prakt. Chemie, **77**, 78 (1908).

[2] Ibid., **74**, 157 (1906); "Die direkte Einführung von Substituenten in den Benzolkern," 1910, p. 211 and following.

an additive-process J. Obermiller [1] believes that it consists in the direct exchange of atoms, and that in the formation of nitrobenzene, for example, the NO_2 group in nitric acid $HO \cdot NO_2$, changes place with the hydrogen atom of the benzene ring and vice versa. In such cases the reactivity of the hydrogen atoms is supposed to be due to their relatively detached positions.[2] Obermiller explains the formation of *ortho-*, *para-*, and *meta*-disubstitution products respectively by assuming that groups like OH, NH_2, etc., increase the reactivity of hydrogen in the *ortho-para* positions and thus tend to orientate substituents in these directions while such groups as NO_2, SO_3H, etc., decrease the reactivity of hydrogen in the *ortho* and *para* positions with the result that the hydrogen in the *meta* positions becomes relatively more reactive and is therefore more readily replaced. Decrease in the mobility of hydrogen in the *ortho* and *para* positions is explained as due to steric hindrance. In order to account for the effect of steric hindrance upon a hydrogen atom in the *para* position to the orientating group Obermiller proposed the use of a new formula for benzene, viz.:

This stands midway between the diagonal formula proposed by Claus and the centric formula of Baeyer and Armstrong, and represents the carbon atoms in both *ortho* and *para* positions as being in direct union with the carbon atom which is holding the orientating atom or group. The peripheral *ortho* bonds represented by solid lines are supposed to be stronger than the diagonal *para* bonds represented by the waving lines.

Obermiller also attempts to explain the effect which *meta*-orientating groups such as NO_2, SO_3H, etc., have upon hydrogen atoms in the *ortho* and *para* positions as due to steric hindrance, but his reasoning and the evidence which he brings forward in support of his reasoning while plausible is sometimes far from convincing.

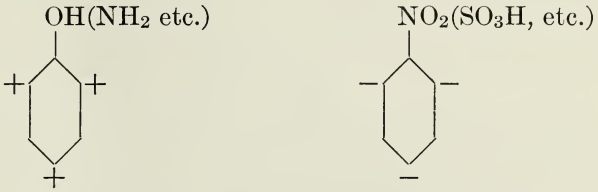
In order to account for the increased chemical activity of hydrogen in the *ortho* and *para* positions Obermiller, like Flürscheim, supposes that groups such as NH_2, OH, etc., which favor substitution in

[1] Jour. prakt. Chem., **75**, 1 (1907); **77**, 65 (1908); **82**, 462 (1910); **84**,449 (1911); J. Obermiller: "Die orientierenden Einflüsse und der Benzolkern," Leipzig, J. A. Barth (1909).

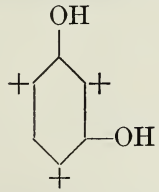
[2] Ibid., p. 40.

this sense, demand a relatively great amount of affinity from the carbon atom with which they are combined, and that as a result the linkages of other atoms in the molecule are weakened in the sense previously described. This weakening effect is most felt by hydrogen atoms in the *ortho* and *para* positions.

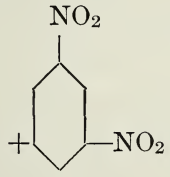
Obermiller represents a relative increase or decrease in the chemical activity of ring carbon atoms by means of the signs + and −. Thus for example:



If two like groups, whether of the *meta*, or *ortho-para* orientating type, are present in the molecule thay may be imagined either as reenforcing or as neutralizing each other. Instances of reenforcement may be found in the case of resorcinol, *m*-phenylene-diamine, *m*-cresol, *m*-xylene, etc. The effect of two *ortho-para* orientating groups is invariably the same and finds expression in the following formula:



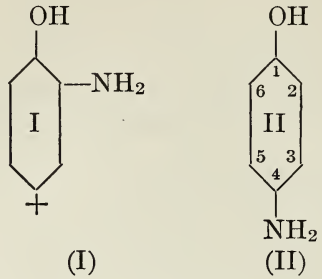
In the case of *m*-orientating groups, however, the effect is quite different and may be represented thus:



Here the tendency to further substitution has been greatly decreased, and while the single hydrogen atom designated by the plus sign is still capable of being replaced it reacts much less readily than in the case of mono-nitrobenzene.

Instances of the complete or partial neutralization of one group by another are to be found among the *ortho* and *para* disubstitution products of benzene. In such cases the relative influence of a given

group may be roughly determined, supposing that the two substituents are different. In the sulphonation of *ortho* and *para*-amidophenol, for example,



(I) (II)

the sulphonic acid group will assume a *para* position to that group which has the stronger power of orientation. In the case of I, for example, it has been found that the hydroxyl group is the more effective since 1, 2, 4-hydroxyamidobenzene sulphonic acid is formed. This conclusion is confirmed by the fact that in the case of II the sulphonic acid group enters the molecule in the *ortho* position with reference to the hydroxyl.

As a result of observations based upon reasoning of this sort Obermiller has arranged the following series as representing the relative strength of different groups:

$$OH > NH_2 > Cl > CH_3 > H$$

He also concludes that NO_2 possesses greater power of orientation than SO_3H and also than OH.[1]

If several substituents are present in benzene it must be assumed that each individually exercises an influence upon the remaining hydrogen atoms, and that this influence tends either to increase or decrease the mobility of these atoms. The resultant of these various influences will determine which hydrogen will be most readily replaced, but the theory of Obermiller stops here and possesses no advantage over any other theory in predicting the position of such a reactive hydrogen atom in the case of a given derivative of benzene. The theory involves, moreover, many supplementary hypotheses in order to harmonize it with the observed facts, and because of this offers nothing that is really fundamental or illuminating. Nevertheless, representing as it does the results of investigation and of long experience, it is frequently suggestive and valuable.

Still other interpretations of the mechanism of substitution are possible on the basis of the valence-electron hypothesis of J. Stark

[1] Jour. prakt. Chemie, 89, 70 (1914); Zeitschr., angew. Chemie, **27**, 37 (1914).

and of the closely related theory of Vorländer. Before attempting a detailed study of these conceptions, however, it seems advisable to pause and consider the so-called laws of substitution in the benzene ring. These rules have been formulated by Holleman on the basis of a large amount of experimental evidence which has been tested and amplified as the result of special investigations by Holleman and his students. This evidence, although far from complete on the quantitative side, is fairly comprehensive and is rapidly receiving additional confirmation as new methods for the quantitative study of organic processes are developed. In brief, Holleman [1] has been able to demonstrate that it is possible to predict with comparative certainty the position which will be occupied by the substituting group in the case of reactions of the type,

$$C_6H_4AB \rightarrow C_6H_3 \cdot A \cdot B \cdot C$$

Attention has already been called to the fact that in the case of the disubstitution products of benzene the position of the second group depends largely upon the chemical character of the group already present in the molecule and only slightly upon the character of the entering group. According to Holleman the same general rule holds in the case of trisubstitution. Three disubstitution products are formed as the result of introducing a second substituent C into the monosubstituted derivative,

$$C_6H_5A$$

These isomers are always present in the reaction mixture although at times in markedly unequal quantities, due to the fact that their respective rates of formation are different. Thus the rate with which the reaction as a whole proceeds is divided among the three isomers in the proportion in which they are respectively formed. If the substituent C is introduced into a second compound

$$C_6H_5B$$

the relative amounts of the *ortho*, *meta* and *para* derivatives, C_6H_4BC, which are formed will be different from those observed in the case of C_6H_4AC, because the relative rates of formation are necessarily different in the two cases.[2]

If the substituent C is introduced into the disubstituted benzene $C_6H_4A \cdot B$, the position which C will assume will depend either not

[1] Die direkte Einführung von Substituenten in den Benzolkern, p. 480 and following, Leipzig, Veit and Co. (1910); also Ber., **44**, 725, 2504, 3556 (1911); Obermiller, Jour. prakt Chemie, **82**, 462 (1910).

[2] Compare with Holleman's speculations regarding the nitration of aniline and its sulphate. Ber., **44**, 725 (1911).

at all or only slightly upon the chemical character of C, and largely upon the nature of A and B. It will depend, in other words, upon the power of A and B respectively to orientate to the *ortho-para* or *meta* positions or both. From the relative amounts of the various isomers corresponding to $C_6H_3A \cdot B \cdot C$, it will be possible to gauge their relative rates of formation and so to observe which positions in the molecule are most readily substituted. Up to the present time, however, the relative amounts of the various products formed in substitution reactions have not been determined with accuracy, and the rates of reaction have not been studied with sufficient care. The selective powers of orientation of the groups A and B are, however, known so that it is possible to say whether a given group will orientate to the *ortho-para*, or to the *meta* positions. In certain individual cases the relative rates of formation of the various isomeric products are also known. On the basis of the facts at his disposal Holleman has succeeded in formulating the following general and special rules governing substitution reactions: [1]

1. The rate of *ortho* and *para* substitution is much greater than that of *meta* substitution.
2. In the case of *ortho-para* orientating groups the rate of substitution varies according to the scale

$$OH > NH_2\,[2] > Cl > I\,[3] > Br > CH_3\,[4]$$

3. In the case of *meta* orientating groups the rate of substitution varies according to the scale

$$CO_2H > SO_3H > NO_2$$

Assuming the accuracy of these generalizations Holleman has attempted to predict which isomers might be expected to form as the main products of a reaction and which as by-products in cases where a substitutent, C, takes the place of hydrogen in a given compound, $C_6H_4A \cdot B$.[5] The results of these prognostications are contained in the following tables.[6] The theoretical and experimental data are arranged in parallel vertical columns and show fundamental agreement:

[1] Holleman: " Die direkte Einführung " etc., pp. 469–70 (1910); also Obermiller: " Die orientierende Einflüsse und der Benzolkern," p. 50 (1909).

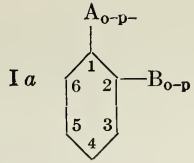
[2] The rate of substitution of OH is greater than that of $-NH \cdot COCH_3$, Obermiller, l. c., p. 54.

[3] It is at present uncertain whether I should come before or after CH_3 in this series. See Holleman, l. c., p. 466.

[4] It may be noted that this arrangement corresponds to that of Obermiller.

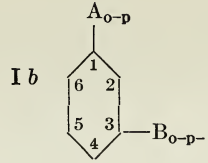
[5] Holleman, l. c., p. 470.

[6] Ibid., pp. 470–74.



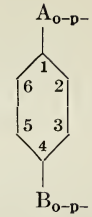
I *a*

Present		C. Enters	
A	B	Exper.	Theor.
Cl	Cl	4, 3	4, 3
Cl	CH_3	4, 6	4, 6
Cl	NH_2	5	5
Cl	OH	5, 3	5
Br	Br	4, 3	4, 3
Br	CH_3	4, 5, 3	4, 5
Br	NH_2	5	5
Br	OH	5, 3	5
I	I	4?	4, 3
I	CH_3	4	4
I	OH	5, 3	5
CH_3	CH_3	4, 3	4, 3
CH_3	NH_2	5, 3	5
CH_3	OH	3 5	5
NH_2	OH	5	5
OH	OH	4	4, 3



I *b*

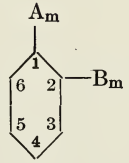
Present		C. Enters	
A	B	Exper.	Theor.
Cl	Cl	4, 2	4, 2
Cl	I	2 oder 6	4, 6, 2
Cl	CH_3	4, 6	4, 6, 2
Cl	NH_2	4 6, 2(?)	6, 4, 2
Cl	OH	4	6, 4, 2
Br	Br	4, 2(?)	4, 2
Br	CH_3	4, 2	4, 6, 2
Br	NH_2	4, 6	6, 4, 2
I	I	4	4, 2
I	NH_2	6	6, 4, 2
CH_3	CH_3	4,2	4, 2
CH_3	NH_2	6, 2, 4	6, 4, 2
CH_3	OH	6, 4, 2	6, 4, 2
NH_2	NH_2	4,(2)	4, 2
NH_2	OH	4, 6 (?)	6, 4, 2
OH	OH	2, 4, 6	4, 2



I *c*

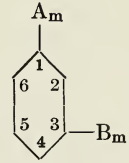
Present		C. Enters	
A	B	Exper.	Theor.
Cl	Br	2	2
Cl	I	2	2
Cl	CH_3	2, 3	2
Cl	NH_2	3	3
Cl	OH	3	3
Br	CH_3	2, 3	2
Br	NH_2	3, 2	3
Br	OH	3	3
CH_3	I	2	2
CH_3	OH	3	3
CH_3	NH_2	3, 2	3
CH_3	OH	3	3
NH_2	OH	3	3
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—

II *a*



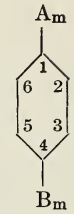
Present		C. Enters	
A	B	Exper.	Theor.
	COOH	4	—
NO_2	COOH	5	4, 6
	COOH	3	—
SO_3H	COOH	4	4, 6
COOH	COOH	3	3
	COOH	4	4

II *b*



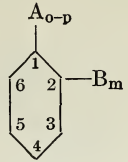
Present		C. Enters	
A	B	Exper.	Theor.
NO_2	SO_3H	5	5
NO_2	COOH	5	5
SO_3H	SO_3H	5	5
SO_3H	COOH	5	5
COOH	COOH	5	5
—	—	—	—

II *c*



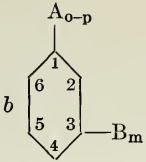
Present		C. Enters	
A	B	Exper.	Theor.
SO_3H	COOH	2	2
NO_2	COOH	3	2
		2	
—	—	—	—
—	—	—	—
—	—	—	—

III *a*



Present		C. Enters	
A	B	Exper.	Theor.
Cl	NO_2	4, 6	4, 6
Cl	COOH	4, 6	4, 6
Cl	CHO	4	4, 6
Br	NO_2	4, 6	4, 6
Br	SO_3H	4, ?	4, 6
Br	COOH	4, 6	4, 6
Br	CN	4	4, 6
I	NO_2	4, 6	4, 6
I	COOH	4	4, 6
CH_3	NO_2	4, 6	4, 6
CH_3	SO_3H	4	4, 6
CH_3	COOH	4, 6	4, 6
CH_3	CN	4	4, 6
NH_2	NO_2	4, 6	4, 6
NH_2	SO_3H	4	4, 6
NH_2	COOH	4	4, 6
OH	NO_2	4, 6	4, 6
OH	SO_3H	4	4, 6
OH	COOH	4, 6	4, 6
OH	CHO	4, 6	4, 6
—	—	—	—
—	—	—	—

III *b*



Present		C. Enters	
A	B	Exper.	Theor.
Cl	NO_2	4, 2	4, 6, 2
Cl	COOH	4, 6, 2	4, 6, 2
Cl	CHO	4, 6, 2(?)	4, 6, 2
Br	NO_2	4	4, 6, 2
Br	So_3H	4, 6	4, 6, 2
Br	COOH	6, 4, 2	4, 6, 2
Br	CHO	4, (2?)	4, 6, 2
I	NO_2	4(?)	4, 6, 2
CH_3	NO_2	4, 6, 2	4, 6, 2
CH_3	SO_3H	6, 5 (?)	4, 6, 2
CH_3	COOH	6, 4, 2	4, 6, 2
CH_3	CHO	4, 2	4, 6, 2
NH_2	NO_2	4, 6, 2	4, 6, 2
NH_2	SO_3H	6, 4	4, 6, 2
NH_2	COOH	2, 4, 6	4, 6, 2
OH	NO_2	2, 6, 4	4, 6, 2
OH	SO_3H	?	4, 6, 2
OH	COOH	6, 2	4, 6, 2
—	—	—	—
—	—	—	—
—	—	—	—

III *c*

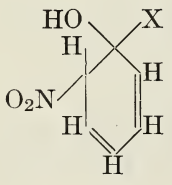
Present		C. Enters	
A	B	Exper.	Theor.
Cl	NO_2	2	2
Cl	SO_3H	2	2
Cl	COOH	2	2
Cl	CHO	2	2
Br	NO_2	2	2
Br	SO_3H	2	2
Br	COOH	2	2
Br	CN	2	2
Br	CHO	2	2
I	NO_2	2	2
CH_3	NO_2	2	2
CH_3	SO_3H	2	2
CH_3	COOH	2	2
CH_3	CN	2	2
CH_3	CHO	2	2
NH_2	NO_2	2	2
NH_2	SO_3H	2	2
NH_2	COOH	2	2
OH	NO_2	2	2
OH	SO_3H	2	2
OH	COOH	2	2
OH	CHO	2	2

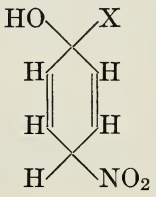
With these and similar considerations as a basis Holleman developed the following hypothesis in regard to the cause and mechanism of substitution:

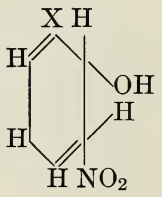
The study of the chemistry of aliphatic compounds has demonstrated the fact that the chemical character of both individual atoms and groups of atoms is very much influenced by their proximity to doubly-bound carbon atoms. Thus for example, in $CH_2{=}CClCH_3$, the properties of the chlorine are very different from those of the chlorine in $CH_2{=}CH \cdot CH_2Cl$, since double decomposition reactions take place much less readily in the former than in the latter case. This influence has been found to be reciprocal, the substituents also affecting the reactivity of the double bonds. Now assuming that Kekulé's formula for benzene is correct, it is obvious that each substituent, X, is in union with an unsaturated carbon atom.

If the same general relations hold in the case of derivatives of benzene as in the case of aliphatic compounds the presence of the substituent X should tend either to increase or decrease the reactivity of the double bond, 1–6. Moreover, its influence upon the conjugated system 1–6–5–4 must also be felt in the sense of either increasing or decreasing 1–4 addition reactions. The double bond 2–3, on the other hand, may be assumed to be only slightly affected by the presence of a substituent in the position shown.

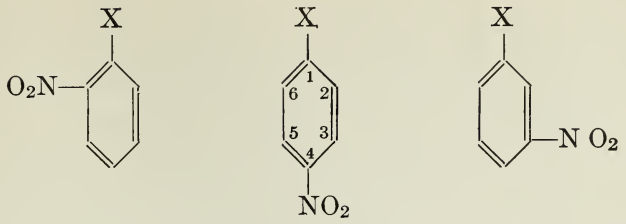
According to Holleman addition reactions may be assumed to precede substitutions. If then C_6H_5X is nitrated three primary addition products are possible, viz.:







This addition is followed immediately by the loss of one molecule of water and the formation of the following disubstituted benzenes:



If the substituent X is such as to favor 1–6 and 1–4 additions, *ortho* and *para* derivatives of benzene will be formed as the principal products of the reaction, while 2–3 additions representing *meta* substitution products will be negligible. If, however, the influence of the substituent is such as to retard this type of addition, 2–3 addition will appear to possess the greater relative velocity and *meta* derivatives of benzene will be formed as the principal products of the reaction. The nitration of phenol and toluene respectively may be considered in illustration. Inspection of the series of orienting groups already referred to shows that the presence of hydroxyl in position 1 has the effect of strongly increasing the chemical activity of the adjacent atoms. This condition favors 1–6 and 1–4 additions, and as a matter of fact the sole products resulting from the nitration of phenol are *ortho*- and *para*-nitrophenol. The substitution of a methoxy for an hydroxyl group in this position decreases the rates with which such additions take place with the result that the reaction mixture contains a small quantity of *meta*-nitromethoxybenzene in addition to the *ortho*- and *para*-derivatives. If the substituent X decreases the reactivity of the conjugate system 1–6–4–5 still more, 2–3 addition may come to predominate and *meta* substitution products of benzene may become the principal products of the reaction.

It is possible in terms of this theory to understand why *meta* substitution products of benzene generally form slowly since 2–3 addition represents addition to a single unsaturated double bond and this type of reaction is generally recognized as taking place with less ease than the so-called 1–2 and 1–4 additions to conjugate systems of double bonds.

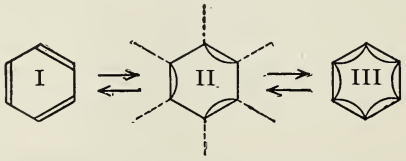
The preceding illustrations serve to show that the quantitative relationships which govern the relative amounts of the different isomers which are formed as the result of substitution vary considerably even in the case of a particular type of reaction. In general, it may be said that the influences which may be regarded as capable of producing variations are (1) the nature of the substituents which are already present in the molecule, (2) the nature of the entering group, (3) external conditions such as temperature, catalyzers, etc.

The fact must again be emphasized that all rules in regard to substitution reactions are purely empirical in character and that their chief importance is to be found in the fact that they serve as a means by which, reasoning strictly from analogy, it is possible to predict the position which a substituting group will assume in a given derivative of benzene. These empirical rules are of especial interest at the present time because they are now capable of a rational interpretation in terms of the electro-chemical conceptions of Stark and Vorländer. Attention has recently been directed to this fact by H. Pauly [1] and his exposition of the matter must now be considered.

Pauly points out that a comprehensive survey of all of the facts in regard to the physical and chemical relationships of benzene and its derivatives which have been developed up to the present time as the result of the most careful investigation of these substances, leads to the following conceptions in regard to the structure of the benzene molecule:

1. The six carbon atoms must all lie in the same plane.
2. They must be bound together in exactly the same way to form a ring which is absolutely symmetrical in all of its arrangements.
3. The ring cannot be assumed to contain either the centric or ethylene type of carbon linkages since all of the bonds between the several carbon atoms must be the same and each must represent a degree of saturation which is more than that of a single and less than that of a double bond between carbon atoms.

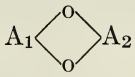
Of the existing formulas for benzene the Kekulé-Thiele formula is the only one which embodies these fundamental conceptions in regard to the relationships which exist between the six carbon atoms. Pauly points out, however, that in accepting it as the final expression for these conceptions the assumption must be made that the symbol ⌓ actually represents a degree of saturation which is more than that of a single and less than that of a double bond. According to this formulation of the matter, the rearrangement from the olefine to the so-called " inactive " condition may be supposed to take place according to the scheme:



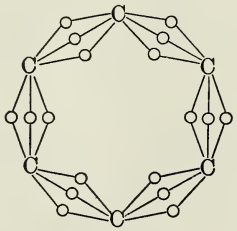
[1] Jour. prakt. Chemie, 98, 118 (1918).

The Kekulé-Thiele formula for benzene when interpreted in this way has the further advantage of being the only formula by means of which it is possible to explain the behavior of benzene and its derivatives in terms of the electron theory. In order to embody the conceptions set forth in the electron theory of J. Stark this formula must, however, be subjected to further slight modifications and when so modified may for convenience be called the Pauly-Stark formula for benzene. In order to understand fully the significance of this name a brief review of certain fundamental facts is necessary.

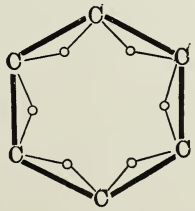
It will be recalled that a simple union between two atoms is represented in terms of the valence-electron theory in the following way:



where the symbol o is used to signify a valence-electron. On the basis of this conception Hugo Kauffmann [1] reasoned that the union of six carbon atoms in a ring might be assumed to take place according to the scheme:

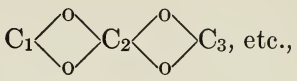


Since, however, a condition such as that which is represented by the above formula must be assumed to result in an immediate redistribution of forces within the molecule and since in terms of Kauffmann's particular conceptions this ultimately leads to a condition of general dispersion of affinity, it seems probable that six electrons become partially dissociated from their respective atoms. This final condition of the benzene molecule may be represented by the formula below:



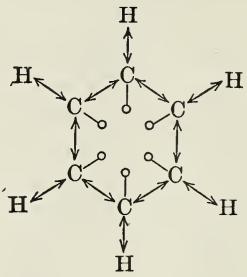
[1] Die Valenzlehre, p. 539.

which not only serves to express the existence of saturated linkages between the six carbon atoms, i.e.,



by means of heavy lines and the presence of partially dissociated electrons by means of the symbol —o—, but also has the additional advantage of resembling the Kekulé-Thiele formula in its main features.

The earlier conceptions of J. Stark in regard to the constitution of benzene found expression in a somewhat similar formula, viz.,



This was, however, superseded by an expression which aimed to give a much more intimate and complete picture of the spacial relationships between the six carbon atoms of the ring, but which at the same time was not sufficiently simple to allow of very general application to the problems involved in the chemistry of benzene. Since this later formula has been embodied to some extent in the conceptions which constitute what has been called the Stark-Pauly formula, it must be considered briefly at this point. It supposes that the six carbon atoms are arranged with their centers of mass at the centers of six regular tetrahedra and with their four respective electrons at each of the four corners. Each atom is so placed with reference to the others that a plane drawn through three of its four electrons is at right angles to a plane of six corners in which lie six electrons belonging respectively to each of the six carbon atoms. Under these circumstances two other electrons, also belonging respectively to each of the six carbon atoms, may obviously be made to fall within two other planes lying above and below the first plane and equidistant from it, while the fourth electron of each of the six carbon atoms will thus come to lie within the first plane but in positions outside the space bounded by the first

six electrons. Fig. 1 attempts to show in perspective the relative positions of three electrons belonging respectively to each of six carbon atoms, the electrons which belong to one and the same carbon atom are joined together by straight lines. The six electrons which lie in the plane of six corners,—which may for convenience be assumed to correspond to the plane of the paper,—are dotted, those lying in a common plane above this are solid black, and those lying in a common plane below the plane of the paper are striped. The bent arrows serve to show that in any given case a dotted electron, as for example, E_{I^3}, is bound to the succeeding carbon atom by means of lines of force which terminate in positive zones located midway between the solid black (E_{II^1}) and the striped (E_{II^2}) electrons of the second atom

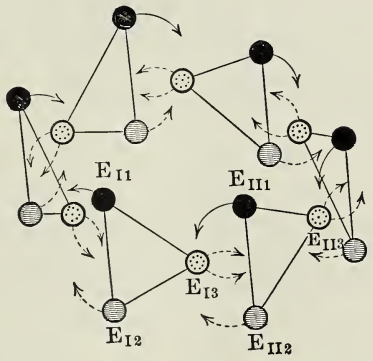


Fig. 1.

E_{II^1} and E_{II^2} are in turn bound to the first carbon atom by means of lines of force which terminate in positive zones located respectively on either side of the dotted electron (E_{I^3}) or, in other words, between E_{I^3} and E_{I^1}, and E_{I^3} and E_{I^2} respectively.

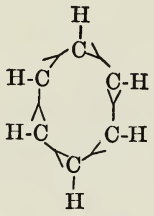
According to this conception, ring formation gives rise to two distinct types of valence fields. Thus E_{I^3}—C_{II}, E_{II^3}—C_{III}, E_{III^3}—C_{IV}, E_{IV}—C_V, E_{V^3}—C_{VI}, and E_{VI^3}—C_I represent practically the same arrangement as has been assumed in the case of single bonds (C—C), while E_{II^1}—C_I and E_{II^2}—C_I, E_{III^1}—C_{III} and E_{III^2}—C_{II}, etc., correspond to the arrangement assumed in the case of triple bonds (C≡C). In the latter case, however, the similarity is much less marked and suffices merely to suggest that the condition which is thus represented as present in benzene results directly from the condition C≡C through the closing of the ring. Thus the two types of union which may be regarded as present in aromatic compounds and in acetylene deriva-

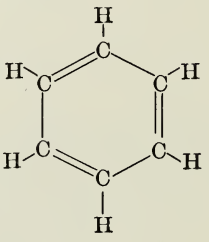
tives respectively, while similar in certain aspects, must be regarded as different in others. This is shown in the relative ease with which the two kinds of union may be ruptured as well as by differences in their energies of formation.

The complexity of the relationship which exists between the six carbon atoms of the ring is apparent when the following facts are considered. It has been calculated that the work required to break the union between E_{I^3} and C_{II} is less than that required to break the single bond between E_I and C_{II}. On the other hand the energy of the 18 electrons which are engaged in ring formation is less than the energy of 18 electrons engaged in maintaining 3 triple bonds plus that of 6 electrons engaged in maintaining 3 single bonds. It is also greater than the sum of the energies required by 18 electrons in maintaining 6 triple bonds. A consideration of these facts led Stark to conclude that the symbols which are used in Kekulé's formula for benzene to represent the nature of the union between the carbon atoms, do not correctly express the facts of the case; he therefore substituted the symbol:

$$C \gtrless C$$

in an effort to show that the union between any two carbon atoms is always the same, and that it corresponds neither to the type of single nor double bonds but is peculiar to ring formation:





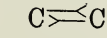
A comparison of the above formulas shows that Stark's expression does not presuppose the existence of isomeric *diortho-* substitution products and, therefore, escapes one of the objections raised against Kekulé's formula. It has the added advantage of being able to account for the observed low heat of combustion of benzene and for the observed difference between the band spectra of benzene and the spectra of substances known to possess ethylene linkages.[1]

Since the stability of the forked single bond, $C_1 \gtrless C_2$, depends upon the presence of identical structures similarly arranged on either side,

[1] Compare Stark, " Die Elektrizität im Chemischen Atom," p. 215.

it obviously cannot exist except in ring compounds. Thus the effect of opening the ring or even of adding two hydrogen atoms to one of the C ≻ C groups, is to render the other forked single bonds unstable and so to bring about their ultimate rearrangement into alternate double and single bonds. For example, when benzene is reduced to cyclohexadiene a ring is formed which contains a system of two conjugate double linkages. This and other related phenomena tend to prove that Stark's theory is in complete harmony with current views in regard to the structural formulas of dihydro- and tetrahydrobenzene and their derivatives.

The relatively great stability of the combinations C ≻ C, as observed in the properties of benzene and its derivatives, is explained by supposing that since the axes of two adjoining carbon atoms always form exactly the same angle with each other, the valence field, C ≻ C, will tend to develop attractive forces which are directed toward the center of the ring and which, in the case of rings containing an even number of atoms, are arranged in pairs the members of which are equal in size but opposite in direction. The fact that the resultants of all centripetal forces in such a molecule act along axes which correspond to the diagonals of a hexagon, tends greatly to increase the stability of this form of combination. It must be emphasized, however, that this reasoning applies only to rings which contain an even number of atoms and that in any given case the relative stability of the ring will depend to a very great degree upon the total number of atoms present in the compound. This follows from the fact that one characteristic angle between the axes of two adjacent carbon atoms is obviously determined by the number of such atoms which are present in the ring and this in turn affects the character of the partial valence field of the forked single bonds. Taking the extreme case of a ring consisting of two carbon atoms,

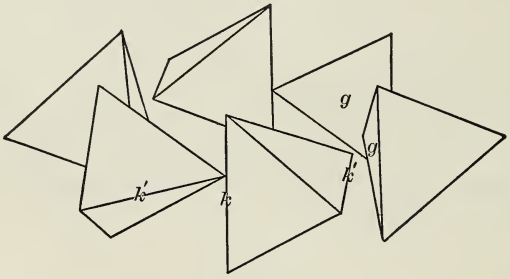


it must be asumed that the common axes of these atoms form an angle of 180° with each other, and that under these circumstances the relationship corresponds to the triple bond of the acetylene linkage. Such a picture serves to explain why acetylene at red heat polymerizes to benzene and why benzene under the same conditions dissociates to give acetylene.

The fact that a six-membered ring possesses much greater relative stability than a four-membered ring is explained by Stark as largely due to the position of the four electrons at the four corners of a

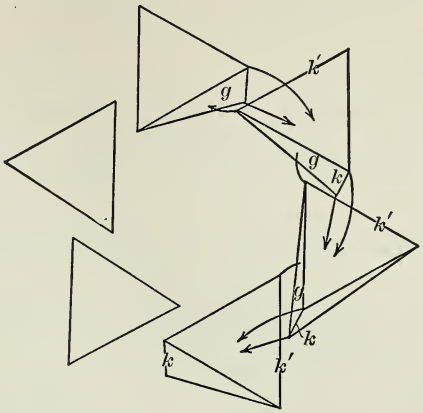
tetrahedron whose center corresponds to the center of mass of the atom.

H. Pauly has recently returned to Stark's original formula for benzene and has made it the basis for further speculation along stereochemical lines. He has thus succeeded in developing a conception which affords a satisfactory interpretation from the standpoint of the chemist of all of the most complicated relationships of benzene and its derivatives. Pauly assumes in the first place that the four valence-electrons which belong to a given carbon atom are located at the four corners of a regular tetrahedron which may be imagined to superinscribe the sphere which bounds the carbon atom in such a way that the surface of the sphere touches four middle points on the four surfaces of the tetrahedron. He further assumes that the six tetrahedra, which represent respectively the six carbon atoms of the benzene ring, are so disposed that one edge (k) of each is vertical to an imaginary plane bounded by a regular hexagon and that in every case k is incident to this plane at points which represent its six corners. If now each tetrahedron is imagined to rotate around its vertical edge until the horizontal edge (k'), which is parallel to the plane of the hexagon, comes to a position directly in front of the vertical edge (k) of the succeeding tetrahedron, a completely symmetrical ring structure will result:



The six horizontal edges (k') of the six tetrahedra will then all lie in a common plane and this plane will also contain the centers of the spheres which represent the six carbon atoms. Those surfaces of the tetrahedra which thus come to face the center of the space bounded by the hexagon, may be pictured as resembling the paddles of a waterwheel. The electrons which are located at the three corners of the above mentioned inner surfaces of the six tetrahedra, in each case come to lie in relatively close proximity to the middle points (positive zones) on the surfaces of adjacent tetrahedra. Fields of force are thus established which operate between the negative electrons and the

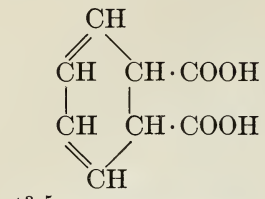
positive zones of the carbon atoms in the manner indicated by arrows in the following diagram:



In comparing these different fields of force it may be assumed that the innermost are the shortest and are, therefore, the strongest. While a " centric grouping " of 12 valence electrons might conceivably result from a slight rotation of the tetrahedra around the vertical axes (k), this would entail the close proximity of the negative charges which are located at the ends of the horizontal edges of adjacent tetrahedra and does not, therefore, recommend itself as a probable arrangement. It would seem more reasonable to suppose that those forces which operate at the center of the ring act in a centrifugal direction while those on the periphery act in a centripetal direction. Such opposing tendencies, which would correspond to the lengthening or shortening of the fields of force, would be expected to equalize ultimately each other when a condition of equilibrium would result. Under these circumstances changes in the distribution of affinity on the different atoms, due to any cause whatsoever, should be accompanied by corresponding changes in the condition of equilibrium within the molecule. This latter conception is obviously of fundamental importance in interpreting the changes which have been observed in the character of the benzene ring itself as a result of substitution reactions and it places the Stark-Pauly electron theory in an exceptional position among the various theories which have been advanced to explain the constitution of benzene.

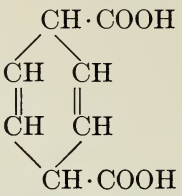
The logical assumption that a connection exists between changes in the equilibrium of the fields of force within the molecule and changes in the properties of benzene and its derivatives, makes it possible to arrive at a satisfactory interpretation of innumerable

reactions. For example, von Baeyer observed that the ease with which the dihydrophthalic acids lose hydrogen to give the corresponding derivatives of benzene differs very considerably. Thus:



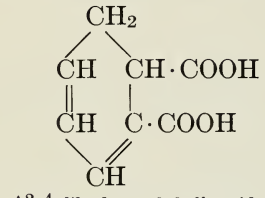
Δ^{3-5} dihydro-*o*-phthalic acid

and



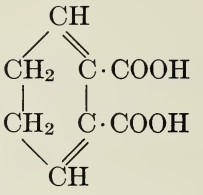
Δ^{2-5} dihydro-terephthalic acid

lose their hydrogen very readily while the corresponding change takes place only with difficulty in the case of



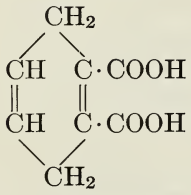
Δ^{2-4} dihydro-*o*-phthalic acid

and



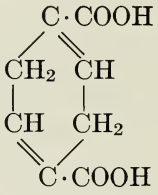
Δ^{2-6} dihydro-*o*-phthalic acid

Finally, no reaction whatever occurs in the case of



Δ^{1-4} dihydro-*o*-phthalic acid

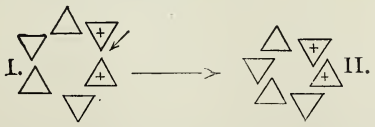
and



Δ^{1-4} dihydro-terephthalic acid

If the above formulas are correct it must be assumed that none of these acids contains a true benzene nucleus. It, therefore, follows that since the benzene condition represents the most stable arrangement of the six carbon atoms of the ring, each acid must in varying degrees possess the tendency to lose hydrogen and pass over into this condition. The change from a diethylene to a true benzene structure must, however, be imagined as taking place with greater ease in cases where the particular carbon atoms of the ring to which carboxyl groups are attached are so placed as to be able to maintain a state of comparative rest during the course of the intramolecular rearrangements. To understand the matter better it is necessary

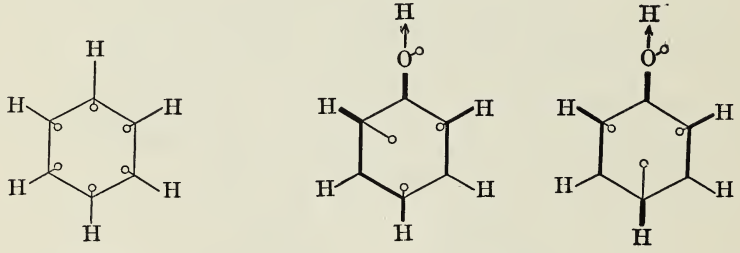
to pause and consider just what readjustments of forces would be involved in such a change. It is apparent in the first place that the loss of hydrogen would be attended by the sudden appearance of free affinity on those carbon atoms to which the hydrogen had been attached and that this free energy would act as a powerful force upon the mass of the neighboring atoms. This would in every case have the effect of drawing these atoms into a closer ring structure by shortening the lines of force already in operation between them. That such a contraction actually occurs as a result of the change has been demonstrated by means of physical measurements. If now under certain conditions this pull upon a given atom is very powerful and is exerted very suddenly, it may act to disrupt the union between this atom and some other atom or group which it is holding, and if, for example, the group should happen to be carboxyl, carbon dioxide might be split off. In such a case the ease with which carbon dioxide would be eliminated might be supposed to depend among other things upon the relative position of the carboxylated carbon atom with reference to the center of the ring. If the atom is far from the center and at the same time is attached to the adjacent carbon atoms by means of single bonds, the change which it suffers will be relatively great and will be accompanied by a loss of CO_2 from its substituent group. If, on the other hand, it is so placed as to be near the center of the ring and in union with one of the adjacent carbon atoms by means of a double bond, the change in position will be relatively slight and the carboxyl group will retain its integrity during the process. These considerations find expression in the fact that both of the first pair of acids whose formulas are represented above, tend to lose CO_2 readily. The fact that Δ^{2-6} dihydrophthalic acid also loses CO_2 although both of its carboxylated carbon atoms are in union with an adjacent carbon atom by means of a double bond, may be understood if the reaction is interpreted by means of the models shown below:



and in which the two carboxylated carbon atoms are represented by the symbol ⧋. A study of these models shows that the transformation from I to II can take place only as the result of a change in the position of at least one of the carboxylated carbon atoms with reference to the other in the sense indicated in the diagram by means of the small arrow.

If similar models are employed to interpret the behavior of the two Δ^{1-4} acids, it is apparent that in neither case is any influence at work which could effect a change in the position of either of the carboxylated carbon atoms. A rearrangement to the benzene condition might, therefore, be expected to take place as the result of readjustments among the other carbon atoms,—the carboxyl groups remaining intact during the process.

The Stark-Pauly electrochemical formula for benzene also possesses the advantage of affording a satisfactory interpretation of the rules which have already been described as governing substitutions in the ring. If Pauly's conception is correct a condition of equilibrium exists among the forces operating between the atoms of the benzene nucleus which corresponds to a very definite and characteristic distribution of affinity. This being the case it is easy to understand why the introduction of a strongly polar atom such as chlorine or oxygen in place of an indifferent atom such as hydrogen should have the power to produce fundamental disturbances. Under these circumstances the force fields within the molecule may be supposed to be affected in either of two ways: (*a*) by the lengthening or shortening of the fields of force acting between the different atoms, (*b*) by the lengthening or shortening of the lines of force acting between a given atom and its unsaturated valence electron. The difference in the distribution of benzene and phenol, for example, finds expression in the following formulas:



Benzene Phenol

where the heavy lines serve to indicate condensed force-fields and where the valence-electrons are represented by the small circles. In interpreting the mechanism by which such a change is effected, it is assumed that the affinity expended by a carbon atom in holding oxygen is relatively much greater than that required for holding hydrogen. The particular carbon atom which is engaged in this way has, therefore, relatively less affinity available for holding the carbon atoms adjacent

to it. This results in a complete readjustment in the affinity relationships of all of the other carbon atoms of the ring, as indicated in the above formulas by light and heavy lines. The presence of partially dissociated (gelockert) valence electrons on the *ortho* and *para* carbon atoms serves to indicate that these atoms are characterized by increased chemical reactivity, since according to Stark's theory electrons of this type are supposed to exercise strong attractions for other atoms.

Since it may be assumed that the action of other non-metallic atoms is similar to that of oxygen and results in the increased chemical reactivity of *ortho* and *para* carbon atoms, this conception affords a satisfactory basis for interpreting the sequence in which one non-metallic element follows another in Holleman's series which is given below and which has been arranged to show the relative strength of different groups in orientating to the *ortho* and *para* positions of the benzene ring:

$$OH > NH_2 > Cl > I > Br > CH_3$$

This arrangement is purely empirical in character, but when it is considered that the strongly polar oxygen atom has the most pronounced influence of any element upon the carbon atoms of the ring, it is easy to understand in terms of Stark's theory why it should be represented in the first group. It is equally easy to see why carbon should be found in the last group since this element, as its position in the periodic system shows, is electro-chemically neutral in character.

The presence of hydrogen in the above groups has no appreciable influence upon the action of the non-metallic atom since hydrogen, like carbon, is what Stark calls an electro-dual element. If, on the other hand, the non-metallic atom, as for example nitrogen, is in combination with one or more strongly polar atoms, as in NO_2, the strength of its union with carbon will obviously be weakened, and this will affect the affinity relationships among the carbon atoms in the ring in such a way as to produce a relative increase in the chemical reactivity of carbon atoms in the *meta*-positions. That the influence of different atoms or radicals which may replace hydrogen in any of the above groups, is relative in character may be seen from a study of the effect of substitution on the orientating power of the methyl group in toluene. As the original hydrogen atoms present in this group are replaced one by one by chlorine, it gradually changes from an *ortho-para* to a *meta* orientating group. This is demonstrated by a consideration of the nitration products which result from the action of HNO_3 upon toluene, mono-, di-, and tri-chlortoluene respectively:

Substituent present in the benzene ring	Position of the entering nitro group
$\overset{1\ 2\ 2\ 2}{\text{—CHHH}}$	2, 4, 3
$\overset{1\ 2\ 2\ 2}{\text{—CHHCl}}$	4, 2, 3
$\overset{1\ 2\ 2\ 2}{\text{—CHClCl}}$	3
$\overset{1\ 2\ 2\ 2}{\text{—CClClCl}}$	3

Other illustrations of the relative effect of atoms of marked polarity upon the orientating power of non-metallic atoms in direct union with ring carbon atoms, are given in the following table:

Substituent present in the benzene ring	Positions of the Different Entering Groups				
	Cl	Br	I	NO_2	SO_3H
$\overset{1\ \ 2\,2}{\text{—C : OH}}$	2, **3**	?	?	**3**, 2	?
$\overset{2\,2\ 3\,3\,3}{\text{—C : OC HHH}}$	?	?	?	**3**, 2, 4	?
$\overset{1\ \ 2\ 2\ 3}{\text{—C}\vdots\text{O O H}}$	2, **3**	**3**	**3**	**3**, 2, 4	**3**, 4
$\overset{1\ \ 2\ 2}{\text{—N}\vdots\text{O O}}$	**3**	**3**	?	**3**, 2, 4	**3**, 2, 4
$\overset{1\ \ 2\,2\,2\ 3}{\text{—S}\vdots\text{OOO H}}$	?	**3**	?	**3**, 4, 2	**3**, **4**
$\overset{1\ \ 2}{\text{—C}\vdots\text{N}}$	?	?	?	**3**	?

It may be noted in this connection that certain groups such as

$\overset{1\ \ 2}{\text{—N=N—}}$, $\overset{1\ \ 2}{\text{—C}\equiv\text{N}}$, $\overset{1\ \ 2}{\text{—CH=CH—}}$, and $\overset{1\ \ 2\ \ 3}{\text{—CH=CH·COOH}}$

do not orientate to the *meta* position. This apparent anomaly is explained by supposing that the influence of nitrogen and carbon in the 2-position is relatively much weaker than that of oxygen. In general, it may be concluded that the orientating power of any group substituting in the benzene ring depends definitely upon the character of the

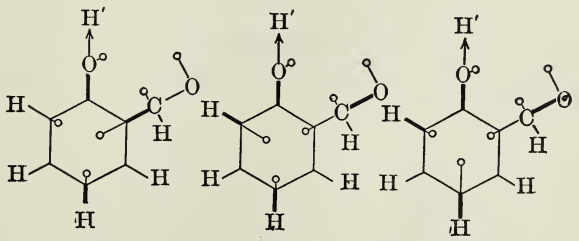
atoms which occupy the 2-positions in the group. The fact that phenyl nitromethane

$$C_6H_5 \cdot \overset{1}{C}H_2\overset{2}{N}O_2\overset{3}{}$$

orientates to the *meta* and not to the *ortho-para* positions might seem at first sight to be in open contradiction to this conclusion, but that this is not actually the case is apparent when it is considered that the nitrogen atom present in the 2-position must here be assumed to be strongly non-metallic in character since it is represented as in union with two oxygen atoms.

Still another contradiction to this rule is to be found in the fact that the group $\overset{1}{-}\overset{2}{Hg}\overset{3}{O}$(Cl, etc.) orientates to the *ortho-para* and not to the *meta* position despite the fact that a strongly polar oxygen atom is present in the 2-position. The seeming anomaly is, however, readily accounted for if the metallic character of the mercury atom is considered, since it then becomes apparent that the polarity of the oxygen might here be insufficient to overbalance the opposing properties of the metal.

The substitution of carbonyl for ring hydrogen results, as might be expected, in an increase in the reactivity of the *ortho-para* positions. In the case of derivatives of those compounds which contain hydroxyl a number of different configurations are possible. If the hydroxyl and carbonyl groups are in union with adjacent carbon atoms, as in salicylaldehyde for example, any one of the following arrangements may result:

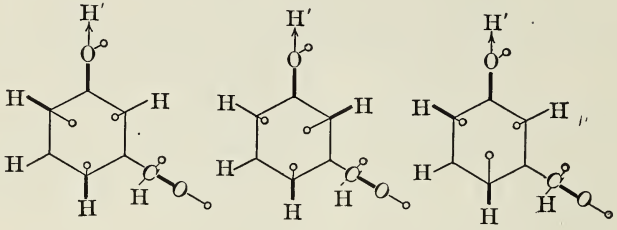


I II III

In the case of I the union between the carbonyl carbon atom and the carbon atom of the ring may be assumed to be unsaturated. Reactivity at this point in the molecule is indicated by the presence of a partially dissociated valence-electron on the ring carbon atom and corresponds to the tendency of the substance (*a*) to lose CO when

heated with sulphuric acid, (*b*) to form 2, 4, 6-tribromphenol when treated with an excess of bromine and finally (*c*) to form catechol when treated with hydrogen peroxide. In the case of the other two formulas (II and III) the reactivity of ring carbon atoms in the 3- and 5-positions with reference to the carbonyl carbon atom is indicated by the presence of a partially dissociated valence-electron at these points in the molecule and corresponds to the tendency of the substance, when in either of these two conditions, to form substitution products in which Br, NO_2, etc., occupy respectively the 3- or the 5-positions.

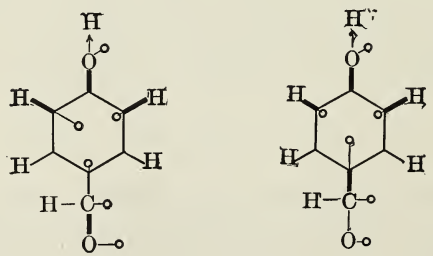
Meta hydroxy-aldehydes may be assumed to possess any of three possible configurations:



I II III

Since none of these formulas indicates the presence of free affinity on the carbonyl carbon atom, such as has been described in the case of one of the possible *ortho*-hydroxy-aldehydes (I), the substance shows no tendency to lose CO under the action of H_2SO_4, H_2O_2 or Br_2. The above formulas indicate, on the other hand, that the substance is distinctly aldehydic in character and, therefore, has a tendency to oxidize readily to form the corresponding acid.

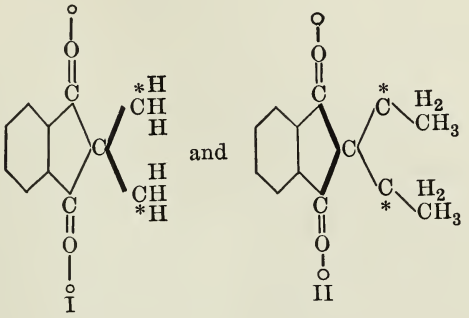
Para hydroxy-aldehydes may be represented by either of two possible configurations:



In cases where the symmetrical arrangement may be assumed, the substance will show a marked similarity to the corresponding *ortho*-

compound (I) and will readily lose CO under the action of H_2SO_4, H_2O_2 and Br_2. Substitution takes place in the positions indicated.

The question as to why the carbonyl group is very reactive in dimethyl α, γ-diketohydrindene (I) and other homologues is one which it is difficult to answer satisfactorily in terms of the older structural theories of organic chemistry but which becomes intelligible from a study of the following formulas:

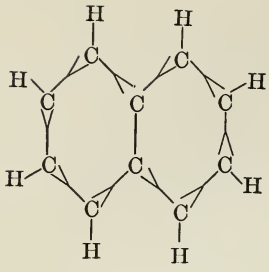


I II

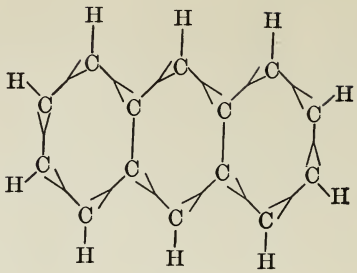
Interpreted in terms of the Stark-Pauly electroatomic theory, it is obvious that in the case of dimethylindandione the carbon atoms of the methyl groups (C*) are strongly bound to the carbon atom of the ring while in the case of diethyl α, γ-diketohydrindene (II) and other homologues this union is weakened because of the carbon atoms of the original methyl groups (C*) are now each engaged in holding a hydrocarbon residue in place of one of the three hydrogen atoms. A comparison of the two formulas shows this substitution of hydrogen is necessarily accompanied by a redistribution of affinity within the molecule and that one result of this is a marked decrease in the reactivity of the carbonyl group. This is indicated by a difference in the relative positions of the partially dissociated valence electrons which are represented as being present on each of the carbonyl carbon atoms.

These illustrations suffice to show the manner in which various phenomena connected with the chemistry of benzene and its derivatives may be explained by means of the valence-electron theory. If, as now seems probable, this theory may be successfully applied to the solution of all problems in the fields of aromatic chemistry, a way will obviously have been opened to a much more intimate understanding of atomic relationships than has ever been possible in the past.

Stark's formulas for naphthalene and anthracene suppose a peripheral arrangement of successive forked bonds (C $\succ$ C $\succ$ C, etc.)



Naphthalene

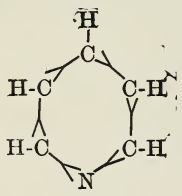


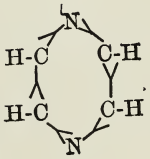
Anthracene

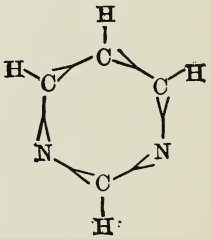
In the case of naphthalene the effect of two condensed benzene rings is produced by means of a single bond (C—C) joining the two central atoms, while in anthracene the presence of three benzene rings is indicated by the presence of two single bonds. In both naphthalene and anthracene the stability of the ring may be assumed to have been decreased as a result of the formation of these single bonds.

These formulas serve to explain differences in the chemical properties of the various derivatives of benzene, naphthalene and anthracene as well as differences in the general stability of these three classes of compounds. Thus, for example, it is easy to understand why carbon atoms in the naphthalene and anthracene rings which are common to two so-called benzene nuclei and which are represented as in union with other carbon atoms in similar positions by means of simple linkages, should possess markedly different properties from carbon atoms which are in union with hydrogen.

Pyridine, pyrazine and pyrimidine may be represented by means of formulas which are similar to that of benzene:







In all of these systems, however, the continuity of the ring is interfered with by the presence of a nitrogen atom. This follows from the fact that the valence fields of nitrogen must be assumed to differ from those of carbon, but, while the resulting structure is less homogeneous than in the case of benzene, it is, nevertheless, capable of considerable stability.

The valence-electron theory is of particular importance to the chemist because it affords a means for establishing a relationship between the optical properties of a given substance and the number and nature of the valence fields which are present in its molecule. This connection is made by assuming that the oscillation of valence fields around given positions of equilibrium on the atoms is electromagnetic in character and is accompanied by the emission and absorption of light. Since, moreover, the waves of light which have their origin in the valence fields of the atoms are assumed to possess the same frequencies as the valence fields, it follows that optical measurements may be used to define the character of the valence fields. In other words, by determining the frequencies and the intensities of the different waves of light which are emitted or absorbed by a given chemical compound, it is possible to draw certain definite conclusions in regard to the nature, strength, and stability of the various forms of union which exist between the valence electrons and the atoms which are present in that particular kind of molecule. It follows, moreover, that the chemical constitution of different molecules may be theoretically deduced from considerations based upon the optical properties of the corresponding compounds.

Stark's theory has been described only in the barest outline, but even so it is apparent that it agrees fundamentally with the electrochemical conceptions of Berzelius. The new theory possesses the advantage, however, of correlating these conceptions with the results of the most recent investigations of physicists in the field of atomic-structure and it, therefore, affords a much more intimate understanding of the interatomic relationships than was possible in Berzelius' time.

Another theory which seeks to interpret atomic relationships has been advanced by D. Vorländer [1] and must now be considered briefly. Vorländer uses the conception of the positive and negative character of atoms and radicals as the vehicle by means of which he ultimately arrives at conclusions which are closely analogous to those which have just been described as deduced by means of the valence-electron theory. It may be recalled that Vorländer [2] was led to assume, as the result of a careful study of a long series of reactions, that NO_2, SO_3H, and COOH function as positive groups in benzene, while NH_2 and OH function as negative groups. He also made the further observation that a benzene carbon atom appears to be negative in character when in union with a positive group and positive in character when in union with a negative group. The relation of these various atomic changes is expressed by means of the following formulas:

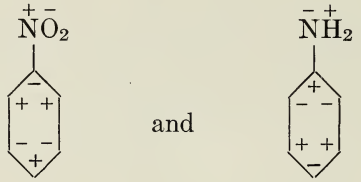
[1] Ber., **52**, 263 and 274 (1919).
[2] Ber., **52**, 263 (1919).

Bz. C. N O_2 Bz. C. N H_2

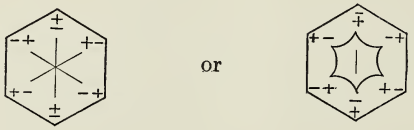
Bz. C. S O_3 H Bz. C. O H

Bz. C. C O_2 H Bz. C. C H_3

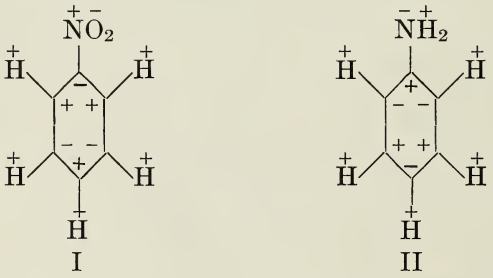
The distribution of the electro-positive and electro-negative charges among the six carbon atoms of the benzene ring is supposed to be different in the case of these two general classes of derivatives and is represented diagrammatically as



In brief Vorländer assumes that the bound and free charges on the carbon atoms of the ring are alternately positive and negative in character:



In cases where the relative difference in potential needs to be expressed still other diagrams are used



I II

In the first formula (I) it will be noted that the positive hydrogen atom of the ring has been replaced by an atom of the same sign and it may, therefore, be assumed that the resulting compound will be relatively stable and that in general it will resemble the parent substance. In the second formula (II), on the other hand, the substituting atom possesses

an opposite charge and the resulting derivative will, therefore, show a marked increase in the potential difference between certain of the carbon atoms of the ring and the atoms which are in union with them. Such a condition may be assumed to be accompanied by an increase in the chemical reactivity of the substance and in cases where the potential difference is very great this may even result in the complete disruption of the ring.

In the formation of disubstitution products as the result of nitration, sulphonation, halogenation, etc., the position taken by the entering group will be one where the ring carbon atom is assumed to possess a negative charge. A comparison of the formulas of nitro- and amino-benzene shows that this will be the *meta*-position in I and the *ortho-para*-positions in II. Thus the rules governing substitution in the benzene ring may be expressed in terms of Vorländer's conceptions in the following way: " in the formation of disubstitution products of benzene by processes of nitration, sulphonation, halogenation, etc., the entering group will be orientated to the *meta* position by the presence of positive elements in the side chain, as for example in the case of $C_6H_5\overset{+}{E}$, and to the *ortho-para*-positions by the presence of negative elements, as for example in the case of $C_6H_5\overset{-}{E}$. The following groups are assumed to have the same effect upon the carbon atoms of the ring as has been described in the case of a positive element:

SO_3H, NO_2, CHO, $CH{=}NO_2H$ (in phenylnitromethane),

COOH, CO_2 alkyl, $CONH_2$, CO alkyl, $CO\cdot COOH$,

$\equiv COH$ (in triphenyl carbinol), CN, CCl_3, $\overset{V}{N}H_3X$,

$\overset{V}{N}H_2$ alkyl X, $\overset{V}{N}H(alkyl)_2X$, $\overset{V}{N}H_2$ acyl X

while the following atoms and groups are assumed to exert a negative influence

F, Cl, Br, I, OH, O-alkyl, O-acyl, $\overset{III}{N}H_2$, $\overset{III}{N}H$-alkyl, $\overset{III}{N}(alkyl)_2$,

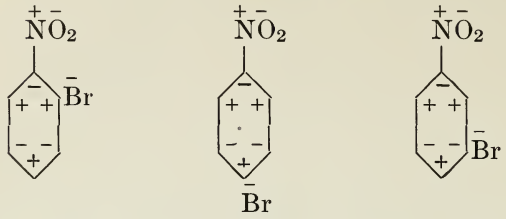
$\overset{III}{N}H$ acyl, $\overset{III}{N}{=}\overset{III}{N}$, CH_3, CH_2 alkyl, $CH(alkyl)_2$, $C(CH_3)_3$,

CH_2Cl, CH_2ONO_2, CH_2SO_3H, CH_2NH_2, CH_2CN, CH_2COOH,

CH_2CH_2COOH, $CH{=}CHCOOH$, $CH{=}CHNO_2$,

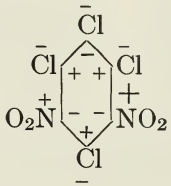
$C{\equiv}C\cdot COOH$, C_6H_5."

If the three nitro-brom derivatives of benzene are examined it will



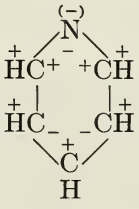
I II III

be observed that the first two compounds in which the negative bromine atom is represented as in union with a positive carbon atom (I and II), contain reactive bromine while the third (III), in which the negative bromine is in union with a carbon atom possessing a like charge, contains indifferent bromine. In other words, *ortho* and *para*-substituted bromine is more reactive than *meta*-substituted bromine, and the same general rule holds for other atoms and groups, as for example, the alkoxyl and alkylamino radicals. In the light of these considerations it is easy to understand why only three of the chlorine atoms present in 1, 2, 4, 6-tetrachlor-3, 5-dinitrobenzene



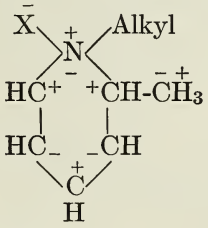
are chemically reactive while the fourth, namely that in the 1-position, is unreactive.

Vorländer's conception lends itself to the satisfactory interpretation of a great many other facts,[1] which are included in Holleman's rules in regard to substitution. This theory may also be applied to explain the close analogy which exists between pyridine and mono-substitution products of benzene as is apparent from a study of the following formula:



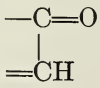
[1] Ber., **52**, 279 (1919); also Meisenheimer, Ber., **53**, 361 (1920).

The only difference is that in the case of pyridine the negative charge on the nitrogen is represented as free while in the case of the corresponding carbon atom in benzene the negative charge is neutralized by the positive charge on a hydrogen atom. The addition of acids and of alkyl halides to pyridine acts to change the charge on the nitrogen from negative to positive. It is easy to understand in terms of this conception why the hydrogen atoms of the methyl group are so reactive in quaternary alkyl derivatives of picoline:

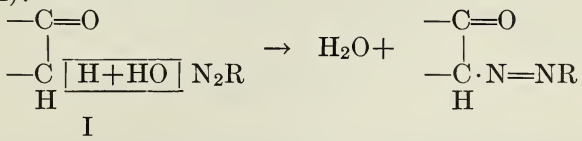


The reader is referred to the writings of A. von Weinberg [1] for a consideration of the kinetic aspects of the subject.

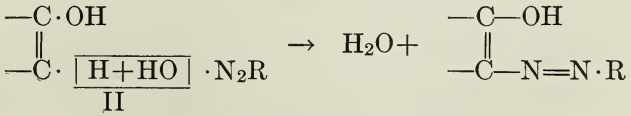
Some very important discoveries have been made recently in regard to the coupling of diazo-compounds with substances which contain the atomic grouping



In the study of this reaction a variety of opinions has been expressed in regard to the mechanism involved in the process. For example, some chemists have regarded the reaction as one of double decomposition in the sense (I):

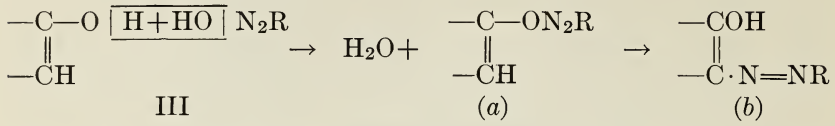


Others have assumed that rearrangements of the *keto* into the *enol* modifications were always preliminary to the coupling of these substances with diazo-compounds. In this case any one of three other equations is possible: II. The hydrogen which is in union with the carbon atom holding the *enol* group may be directly substituted



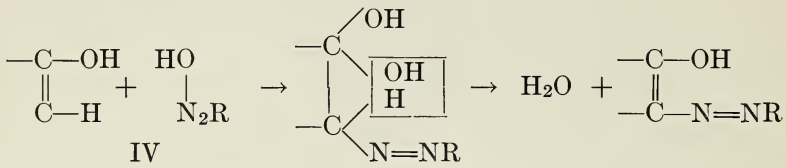
[1] Ber., **52**, 928 and 1501 (1919).

III. The hydrogen of the *enol* group may itself react in which case an ether of diazobenzene would be formed as a primary product, but would probably rearrange to give a true azo-compound:



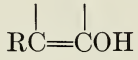
III (*a*) (*b*)

IV. Addition of the diazo-compound may take place as the primary reaction and this may then be followed by the splitting off of water:

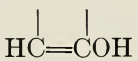


IV

In an effort to reach a decision in this matter O. Dimroth [1] investigated the action of diazo-compounds upon desmotropes such as acetyldibenzoylmethane, tribenzoylmethane, mesityloxidoxalic ester, α and β diacetosuccinic ester, etc. His results showed that the *enol* form reacted in every case while the *keto* modifications were entirely inert. This eliminates the first equation (I) as affording a possible interpretation of the mechanism of this reaction. The second equation (II) can also be discarded since it has been observed that substances which contain the combination



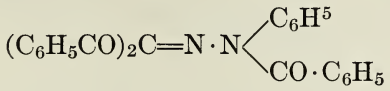
couple with diazo-compounds as readily as substances which contain the combination



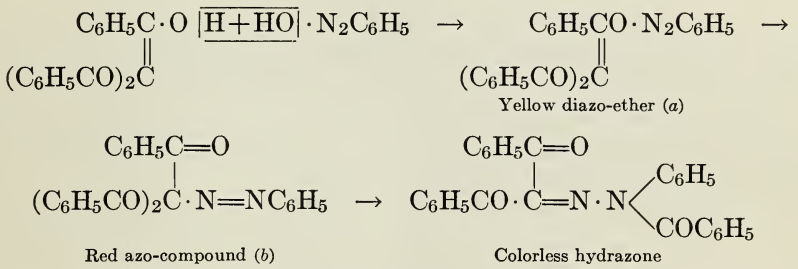
This narrows the number of possibilities to the last two equations, and of these IV was rejected and III accepted as a result of the following considerations: It was observed that the *enol* modifications of tribenzoylmethane reacted with diazo-compounds to give a yellow product and that this upon heating was transformed first into a red and then into a white substance. The yellow addition product behaves like a true diazo-compound in that it decomposes with the evolution of nitrogen when boiled with alcohol. It also resembles a true diazo-compound in that it couples with β-naphthol, and on reduction gives a mixture of

[1] Ber., **40**, 2404, 4460 (1907); **41**, 4012 (1908).

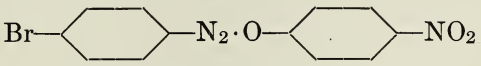
phenylhydrazine and tribenzoylmethane. The change from a yellow to a red compound on heating may be interpreted as due to the formation of an azo-compound (III*a* → III*b*). The change from the red to the colorless isomer is somewhat more difficult to formulate, but has been explained by Dimroth as due to the formation of the benzoylphenylhydrazone of diphenyltriketone.



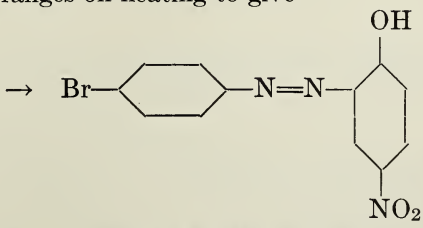
The mechanism of the complete reaction may therefore be formulated as follows:



Dimroth and Hartmann have succeeded in isolating a number of ether like bodies which form as intermediate products in the process of coupling diazo-compounds with phenols. These also rearrange upon heating to give what seem to be the corresponding azo-compounds. For example *p*-brombenzene-diazonium chloride couples with *p*-nitrophenol to give the oxygen derivative:



and this then rearranges on heating to give

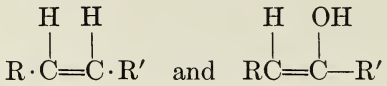


p-brombenzene-azo-p-nitrophenol

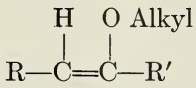
These investigations of Dimroth and his students have helped to simplify the problem by limiting the number of interpretations which are possible in explaining the mechanism of these reactions. They

have also served to bring out the analogy between the action of diazo-compounds upon phenols and upon amines.

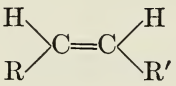
Further important contributions to the same general problem have been made by Kurt Hans Meyer. These developed naturally as a result of Meyer's investigations in the field of *enol-keto* tautomerism,[1] in the course of which he discovered that the *enol* group is one of the most reactive complexes known in organic chemistry. For example, if compounds of the general formulas



are compared it is found that those belonging to the second class react much more readily with bromine, nitrous acid, aldehydes, etc., than those of the first class. This increased activity cannot be due to the mobility of the *enol* hydrogen since this may be replaced by alkyl without affecting the reaction. Thus K. H. Meyer and Lenhardt have found that *enol* ethers of the general formula



are just as reactive as the free *enol* combination. They have also demonstrated that in neither case is the reactivity due to the presence of negative groups in the molecule nor to any tendency of the substance to ionize. They conclude, therefore, that it must be a function of the ethylene linkage and assume that the reactivity of this part of the combination



is enormously increased by the substitution of OH or of OR. This type of ethylene linkage is referred to by Meyer as " an *active* double bond." [2]

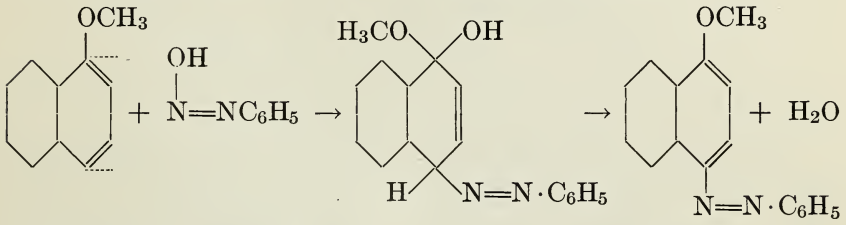
In the course of these investigations Meyer made the remarkable discovery that diazo-compounds couple as readily with phenol-ethers as with the free phenols, and that in the former case addition takes place without the splitting off of alkyl groups. Meyer succeeded in

[1] Annalen der Chemie, **380**, 212 (1911); **398**, 49 (1913); Ber., **44**, 2718 (1911); **45**, 2843 (1912) Ber., **47**, 1741 (1914).

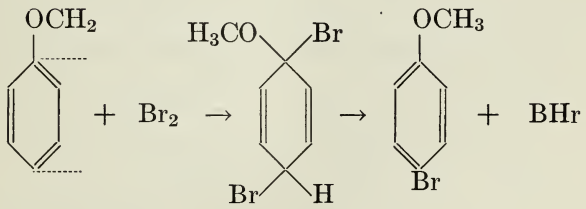
[2] Annalen der Chemie, **398**, 71 and 80 (1913).

preparing well-defined addition products in the case of a large number of phenol-ethers so that the reaction came to possess general significance. It was, moreover, attested to by other investigators.[1]

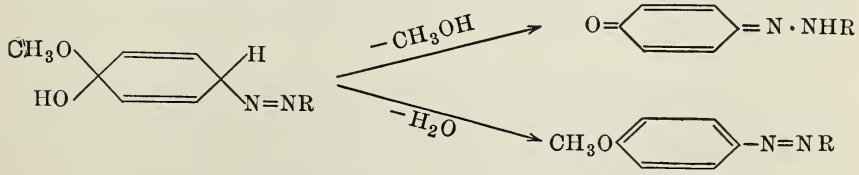
These discoveries make it impossible to explain the mechanism of the reaction by supposing that it takes place with the formation of diazo-ethers as intermediate products, since this would involve the hydrolysis of the phenol ether and it has been observed that alkyl groups are not split off during the process of coupling. It would, therefore, seem to follow that coupling in such cases must represent the addition of the diazo-body to a so-called *active* double bond.



The process of coupling thus appears to be exactly analogous to bromination:



Under certain circumstances the addition product may lose alcohol instead of water in which case oxazo-compounds are formed. Indeed both reactions may take place simultaneously as is expressed by the following equations:

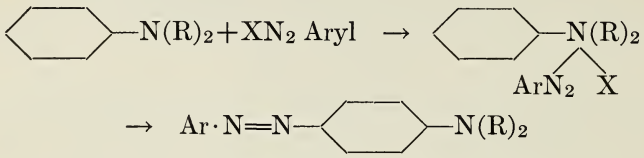


P. Karrer[2] has recently observed that alkyl groups are sometimes split off during the process of coupling diazonium salts with tertiary

[1] K. von Auwers and Michaelis, Ber., **47**, 1275 (1914).

[2] Ber, **48**, 1398 (1915).

amines. Thus, for example, the amyl group is eliminated when N-diisoamyl aniline is used in the reaction. In order to explain this phenomenon Karrer assumed that the reaction took place in two stages, the first of which involved direct addition to the nitrogen. The addition product which was formed in this way was then supposed to undergo rearrangement to an azo-compound. Under normal conditions rearrangement was accompanied by the elimination of one molecule of halogen acid but under other conditions the elimination of a molecule of alkylhalide was assumed to be possible.



This phenomenon is obviously analogous to that which has been described as taking place in the case of certain phenols and phenol ethers. The reaction in the latter case was, therefore, explained by assuming that the product which is formed by the primary addition of the reacting molecules belongs to the class of quaternary oxonium compounds. Since addition products which are formed in this way are in their nature difficult to isolate, the reaction has recently been studied from the standpoint of kinetics by A. Skrabal [1] and O. Dimroth.[2] The data which were obtained as a result of measuring the rates of reaction in the case of a number of different phenols, showed that the velocity with which coupling takes place varies greatly and that it seems to depend both upon the nature and the position of the group substituting in the phenol.[3] Thus, for example, weakly acidic phenols with substituents in the *ortho-* and *para*-positions react with great ease to form diazo-ethers but do not give azo-compounds. The fact that the formation of azo-compounds thus seems to depend upon the presence of ring hydrogen in the *ortho-* and *para*-positions tends to support Karrer's view that these substances result from a process of intramolecular rearrangement.

These facts have, however, been interpreted in quite a different manner by K. H. Meyer, who assumes that in both types of coupling which have been described, addition depends upon the presence of unsaturated ethylene linkages and not upon the presence of hydroxy or amido groups. According to this conception it should be possible to

[1] Monatsh., Chemie, **37**, 137 (1916); **38**, 29 and following (1917).
[2] Ber., **50**, 1534 (1917).
[3] Compare Auwers and Borsche, Ber., **48**, 1716 (1915).

couple unsaturated hydrocarbons with diazo-compounds. Acting upon this hypothesis Meyer has in fact made the remarkable discovery [1] that hydrocarbons such as butadiene, $CH_2{=}CH\cdot CH{=}CH_2$; α-methylbutadiene, $CH_3CH{=}CH\cdot CH{=}CH_2$; and β-γ-dimethylbutadiene, $CH_2{=}C(CH_3)\cdot C(CH_3){=}CH_2$, are able to couple with nitrobenzene diazonium hydrate in acetic acid, in alcohol, and even in aqueous solution, to give true azo-compounds. A very careful investigation of the product derived from β-γ-dimethylbutadiene showed that it corresponded to the formula

$$O_2N\cdot C_6H_4N{=}N\cdot CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}\text{——}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$$

and that it closely resembled the aromatic azo-compounds in its chemical properties. Since butadiene also reacts readily with diazotized dinitroaniline to give a true azo-compound, namely,

$$(NO_2)_2C_6H_3N{=}N\cdot CH{=}CH\cdot CH{=}CH_2$$

the reaction cannot be explained on the assumption that it is due to the reactivity of a methyl group which is in union with ethylene carbon. The explanation brought forward by Meyer supposes that the transformation takes place according to the following scheme:

$$\begin{array}{l} CH_3CH\ldots \\ \quad\| \\ \quad CH_2\ldots \end{array} + \begin{array}{l} HO \\ \quad| \\ \quad N{=}N\cdot R \end{array}$$

$$\rightarrow \begin{array}{l} CH_3\cdot CHOH \\ \quad| \\ CH_2\cdot N{=}N\cdot R \\ \quad\quad I \end{array} \rightarrow \begin{array}{l} CH_3\cdot CH \\ \quad\| \\ CH\cdot N{=}NR \\ \quad\quad II \end{array} + H_2O$$

although it was never actually possible in any given case to effect a separation of the intermediate product represented by the first (I) of the above formulas.

Meyer is strongly of the opinion that while it is desirable to be able to use a single type of transformation for the interpretation of all coupling reactions, it is not possible to do this at the present time since at least two general types of reaction occur:

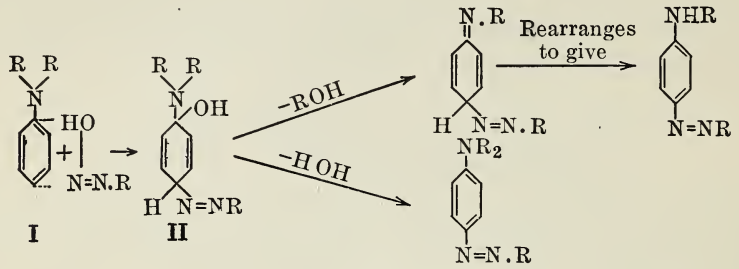
I. Coupling by means of oxygen and nitrogen, with the formation of an ammonium or oxonium salt.

II. Coupling by means of unsaturated carbon linkages.

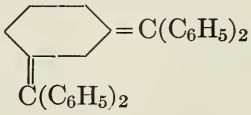
[1] Ber., **52**, 1468 (1919).

The particular type of reaction which occurs in any given case can be determined only as the result of experiment.

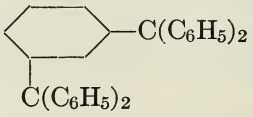
The coupling of tertiary amines with diazonium salts is interpreted by Meyer as belonging to the second, and not, as Karrer assumes, to the first type of reaction and is represented as taking place according to the scheme:



The question as to the possibility of the existence of *meta*-quinoid derivatives of benzene has been reopened in recent years as a result of the investigations of O. Stark [1] who has obtained a hydrocarbon by the reduction of tetraphenylmethoxylene dichloride, to which he has assigned the following formula:



The correctness of this expression has been challenged by W. Schlenk and M. Brauns,[2] who maintain that this hydrocarbon reacts in a manner which is characteristic of triphenylmethyl and its derivatives and that it therefore corresponds to the formula



This discussion fails, however, to bring the question of the existence of *meta*-quinoids to a satisfactory settlement.[3]

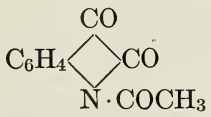
[1] Ber., **46**, 659, 2252, 2542 (1913); **47**, 125 (1914).
[2] Ber., **48**, 661, 716 (1915).
[3] Compare E. Bamberger, Ber., **48**, 1354 (1915).

CHAPTER XI

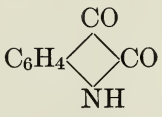
TAUTOMERISM[1] AND DESMOTROPISM

In the course of the development of structural organic chemistry the rule was formulated that every pure organic compound possesses a fixed and definite configuration, and that this particular arrangement of atoms within the molecule can be expressed by one and only one structural formula, assuming of course that no stereoisomerism is possible. Such a constitutional formula was supposed to express the collective reactions of the substance. In 1880, however, individual exceptions to this rule came to be recognized.

In 1882 A. von Baeyer and Oekonomides[2] discovered that isatin, $C_8H_5O_2N$, when treated with acetic anhydride gives an acetyl derivative in which the acetyl group is in union with nitrogen and which, on the basis of its synthesis and properties, possesses the formula:

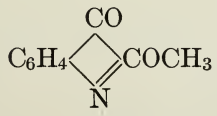


Reasoning from this fact, isatin itself should have the formula I.



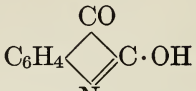
I

Now free isatin gives a mono silver salt which when treated with methyl iodide passes into an imido ester having the formula:



[1] Schaum, Annalen der Chemie, **300**, 205 (1898).
[2] Ber., **15**, 2093 (1882); **16**, 2193 (1883).

from which it follows that isatin itself should possess the isomeric structure containing an hydroxyl group as represented in formula [1] II,

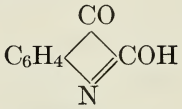


II

According to all previous experience these two formulas, I and II, should correspond to two separate and distinct chemical substances which form as the result of replacing the acetyl and methyl respectively by hydrogen. Observation has proved, however, that one and the same chemical individual, namely isatin, is obtained in both cases. It follows therefore, that this cyclic compound is capable of reacting in the sense of two different but isomeric formulas, *lactam* and *lactim*, or in other words it possesses a dual nature.

Baeyer and his students further made the discovery that this property of isatin is due to the activity of a hydrogen atom not in the benzene ring, and that such a phenomenon ceased to be observed after this particular hydrogen had been replaced by other substituents.

As a result of his experiments Baeyer became convinced that isatin itself possesses the *lactim* formula



but that, in the course of certain reactions, it is transformed into an isomeric compound corresponding to the *lactam* formula, and that this then reacts to give derivatives of the latter type. Baeyer called this supposedly unstable isomer the *pseudo* form of isatin.

Similar phenomena were observed by Baeyer and Comstock [2] in the case of oxindole, by von Pechmann in the case of hydroxynicotinic acid,[3] by Hantzsch in the case of methyl *pseudo*-lutidostyril,[4] by Knorr and Antrick in the case of hydroxyquinaldine,[5] and by Friedländer and Weinberg in the case of α-hydroxyquinoline (carbostyril).[6] In general, Baeyer's idea of a *pseudo* form was accepted and abnormal products were regarded as derived from it. This view involved the assumption

[1] Heller has recently discovered another isomer of isatin. See Ber., **49**, 2757 (1916); **50**, 511 (1917).

[2] Ber., **16**, 1704, 2188 (1883).

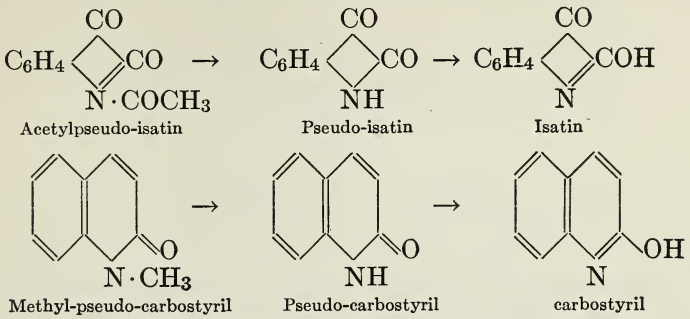
[3] Ber., **17**, 2387 (1884); **18**, 317 (1885).

[4] Ber., **17**, 1026, 2903 (1884).

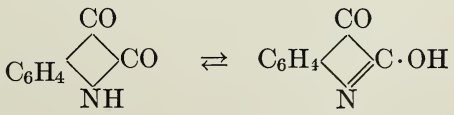
[5] Ber., **17**, 2873 (1884).

[6] Ber., **18**, 1528 (1885).

that such *pseudo*-compounds actually exist momentarily but rearrange almost instantly into normal or stable forms:



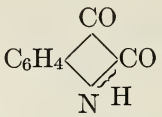
Conrad Laar[1] immediately advanced a quite different interpretation based on the assumption that one and the same chemical individual may possess two or more different structural formulas. This explanation is plausible since all observed phenomena of this type may be accounted for on the assumption that a hydrogen atom is continually moving from one position to another within the molecule and that this change involves a rearrangement in the affinity relations existing between the other atoms. The hypothesis is moreover supported by the following considerations: according to the kinetic theory of gases the atoms within the molecules as well as the molecules themselves are supposed to be in a state of constant motion. The hydrogen atom in particular is regarded as possessing a relatively great mean velocity and as being extremely active. There will be a characteristic oscillation of the atom only in the case of gaseous molecules, while in all other states of aggregation a more or less irregular movement forward and back may be imagined as resulting from constant encounters with other atoms.[2] Even in solid substances, however, the motion of the hydrogen atom may, under certain conditions, become regular and in a sense like the motion of a pendulum. The two atomic groupings within the molecule, which may be imagined as representing the extremes of atomic movements of this type, would thus appear and disappear periodically, and in the case of isatin, might be represented by the scheme:



[1] Ber., **18**, 648 ((1885); Ber., **19**, 730 (1886); Kekulé, Annalen der Chemie, **162**, 77 (1872); Butlerow, Annalen der Chemie, **189**, 77 (1877); Erlenmeyer, Ber., **13**, 309 (1880); **14**, 320 (1881); Knorr, Annalen der Chemie, **279**, 212 (1894).

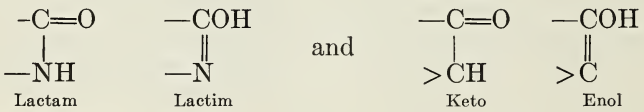
[2] Ber., **19**, 732 (1886).

Thus the substance isatin could be regarded as possessing both of these formulas, or possibly one representing a mean of these two conditions, viz.,



Moreover since the constitution of a substance cf this type changes periodically, it readily passes into derivatives having one or the other formula.

Different structural formulas in such cases indicate not isomeric substances but a single substance having a dual nature, and in order to distinguish this particular phenomenon Laar called such hypothetical isomers, *tautomers*. All observed cases of tautomerism were systematically arranged under classes of the so-called *diads* and *triads*. In general, the atomic groupings which exhibit most frequently this behavior are the following:



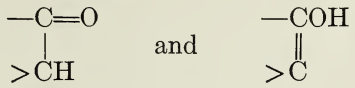
While the word tautomerism has become well intrenched in organic chemistry Laar's particular interpretation of the phenomena has not, however, found universal acceptance among chemists. On the contrary it has been generally assumed that tautomeric substances frequently possess definite constitutions, but that these groupings undergo change during the course of certain reactions. P. Jacobson [1] has, therefore, proposed the term *desmotropism* as offering a more suitable expression than that suggested by Laar.[2]

A. Hantzsch and F. Herrmann [3] are of the opinion that the terms tautomerism and demotropism may both be used to advantage, the former to denote the fact that a given chemical compound exhibits a dual nature, and the latter to signify that a complete and definite rearrangement of affinities within the molecule has actually taken place. According to this conception the formulas representing different desmotropic conditions bear the same relation to each other as do the formulas of isomeric substances. Desmotropism may be distinguished readily from isomerism by the characteristic that only one desmotropic modi-

[1] Ber., **20**, 1732 (1887); **21**, 2628 (1888).
[2] Compare Michael, Annalen der Chemie, **363**, 20 (1908).
[3] Ber., **20**, 2802 (1887).

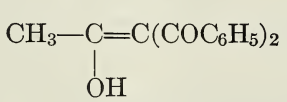
fication is stable under a given set of physical conditions, so that a change in the physical conditions is necessary in order to insure the stable existence of the second isomer. This is true at least of desmotropic substances in the solid state.

In 1896 L. Claisen,[1] W. Wislicenus,[2] and others succeeded in isolating pairs of isomers corresponding to the atomic groupings



These substances, which in many cases had previously been regarded as desmotropic in character, were now found capable of existing in two forms and both modifications were found to be stable under ordinary conditions. In fact, in many instances they were readily transformed one into the other.

For example, Claisen obtained a substance by the action of benzoyl chloride upon the sodium salt of benzoylacetone, which corresponded in chemical properties to the formula:



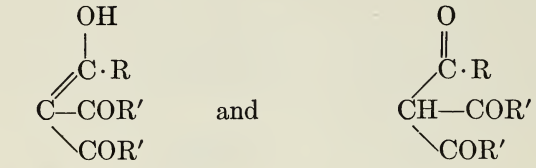
This compound melted at 101–102°, decomposed alkali carbonates in the cold, and when dissolved in alcohol and treated with ferric chloride gave a red coloration indicating the presence of a free hydroxyl group. When this strongly acidic body was heated at 80°–90°, or when crystallized from hot dilute alcohol, it immediately rearranged to give another substance which melted at 107–110°. This new compound was found to have the same percentage composition and the same molecular weight as the original, but corresponded in chemical properties to the true ketone combination represented by formula, $CH_3CO \cdot CH(COC_6H_5)_2$. Thus while the product melting at 101–102° was strongly acid in character, dissolving in alkali carbonates in the cold, the compound melting at 107–110° was neutral and not only did not react with alkali carbonates but did not even react with potassium hydroxide. Upon long standing with alkalies the new substance, it is true, slowly passed into solution, but when this solution was acidified, the isomeric acid melting at 101–102° was precipitated. It was thus possible by simply heating, or by crystallization from hot alcohol, or by solution in alkali and subsequent precipitation, to pass at will from one modification to the other.

[1] Annalen der Chemie, **291**, 25 (1896).
[2] Annalen der Chemie, **291**, 147 (1896).

Thus it was demonstrated that substances having the desmotropic formulas

could be prepared, could exist side by side under ordinary conditions, and finally could be transformed one into the other.

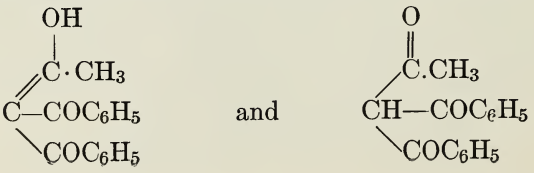
Claisen succeeded in isolating similar pairs of isomers in the case of many other desmotropic substances and observed characteristic differences in the chemical properties of the two modifications. Substances containing hydroxyl groups were referred to as the *enol*, and those containing carbonyl as the *keto* forms respectively. Structurally the two modifications of this series of ketones may be expressed as follows:



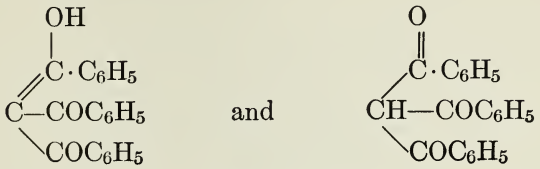
Enol-form (α-form) Keto-form (β-form)

In general, the *enol* modifications were found by Claisen to be strongly acidic and soluble in carbonate solution with effervescence. They also gave a red coloration when allowed to interact with ferric chloride and reacted directly with diazobenzene. The *keto* modifications, on the other hand, are neutral compounds and insoluble in alkali carbonate solution but soluble in cold solutions of strong alkalies. On long standing in alkaline solution at ordinary temperature the *keto* forms undergo intramolecular transformation into the *enol* modifications. In other words there is a tendency for such molecules to become acidic. This arrangement is accelerated by the application of heat. The *keto* forms give no coloration with ferric chloride solution and fail to react with diazobenzene.

Tautomeric compounds having the above general formulas show great variation in stability and this seems to depend upon the nature of the substituents represented by R and R′. Thus both isomers, in which R represents the methyl group and R′ the phenyl radical,

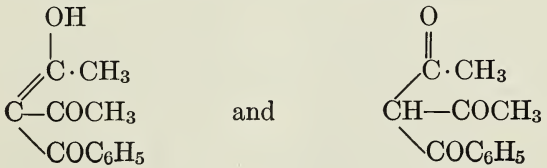


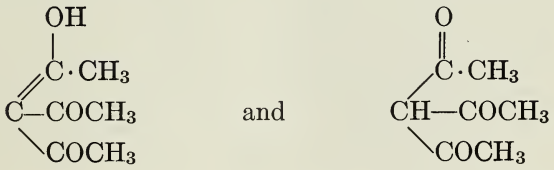
are capable of existing side by side for a long time in the solid state, the *enol* passing into the *keto* form at room temperature only after the lapse of weeks. In the case of the corresponding phenyl derivatives (R and R′=phenyl),



the *enol* modification is so unstable that it is exceedingly difficult to isolate. Even in the solid state and at room temperature it changes into the *keto* form in the course of two days.

Other combinations corresponding to the formulas





exist only in the *enol* form, the isomeric *keto* modification being usually unstable even at ordinary temperatures. In other words unsaturation or increase in negative character of the radicals R and R′ seems to favor the existence of tautomeric isomers.

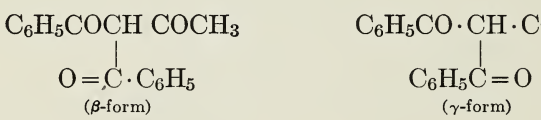
Comparisons of this kind have led to the formulation of more or less definite conclusions in regard to the influence exercised by various radicals upon the relative stability of the atomic groupings. Claisen has shown conclusively that in the series

$$CHA_3,\ CHA_2B,\ CHAB_2,\ CHB_3$$

where A represents an acetyl and B a benzoyl group, the first two are stable only in the *enol* form, the third exists in both modifications, while the fourth possesses a stable *keto* but an unstable *enol* form. Assuming the acetyl group to be more strongly acid in character than benzoyl, it may be said in the words of Claisen that the formation of the *enol* form

is favored both by the negative character of the acetyl groups and by the number of such groups in union with the methane carbon atom.[1]

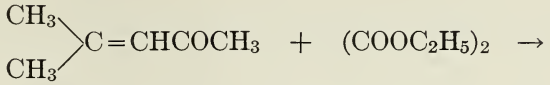
While these assumptions of Claisen have received strong experimental support they have, nevertheless, been challenged by able critics. Among the latter is Michael,[2] to whom the assumption that acetyl is more negative than benzoyl has from the beginning seemed very improbable. Michael holds that the stability of an *enol* form does not necessarily increase with increase in the number of negative radicals, and has suggested another explanation of the phenomena of desmotropism and mesotropism which is based entirely upon considerations of the law of entropy or neutralization law. Michael[3] has recently shown that the *keto* combinations examined by Claisen are capable of existing in more than two isomeric modifications. For example, acetyldibenzoyl methane[4] and the corresponding propionyl compound[5] exist in three different modifications namely: the *enol*, a liquid form, and two *keto* forms (β and γ). The *keto* form (β) in the case of the acetyl compound[6] melts at 107–110° while the γ-isomer is also solid and melts at 146–149°. The β form of the propionyl derivative melts at 122.5° while the γ-isomer melts at 152–3°. The latter is slowly transformed into its β-isomer at 100° and is much less easily enolized than the β form. In the case of the acetyl compound the two isomeric *keto* forms undergo a reversible reaction without enolization in acetic acid, acetic anhydride, and methyl iodide. The isomerization of these types of compounds is probably connected with the spacial arrangement of the atoms in the molecule and is due, according to Michael, to hindered rotation of the benzoyl group on the asymmetric carbon —CH— as expressed by the structural formulas below:

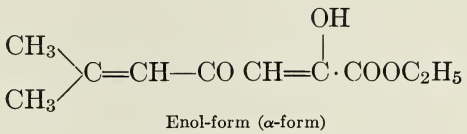


Claisen[7] also observed in his later researches that the condensation product formed by interaction of diethyl oxalate with mesityloxide exists in isomeric modifications. Each is capable of passing into the

[1] Annalen der Chemie, **291**, 37 (1896).
[2] Annalen der Chemie, **363**, 24 (1908); compare K. Meyer, Ber., **45**, 2849 (1912).
[3] Annalen der Chemie, **390**, 30 (1912).
[4] Annalen der Chemie, **390**, 46 (1912).
[5] Annalen der Chemie, **390**, 68 (1912).
[6] Claisen, Ber., **27**, 3182 (1894); Knoevenagel, Annalen der Chemie, **281**, 62 (1894).
[7] Annalen der Chemie, **291**, 39 (1896).

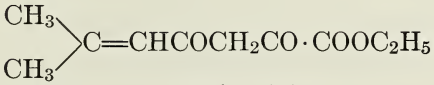
other and their relationships may therefore be expressed structurally by the formulas:





Enol-form (α-form)

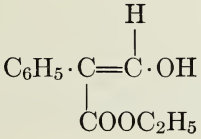
and

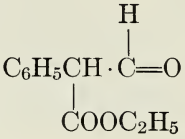


Keto-form (β-form)

The *enol* modification is stable at temperatures above 100° and interacts with ferric chloride giving a red coloration. The *keto* form, on the other hand, is stable only below 100° and does not interact with ferric chloride.

Wislicenus [1] discovered as early as 1887 that ethyl formylphenylacetate, resulting from the condensation of ethyl formate with ethyl phenylacetate, exists in two isomeric forms which readily rearrange each into the other. These isomers have received much attention and later investigation seems to show that they also are structural isomers of the *enol-keto* type:[2]





In the case of these substances the relationships are not quite as simple as in the case of the triacetyl derivatives of methane and as a result certain abnormalities appear. Thus the β-form dissolves more readily than the α-form in sodium carbonate solution even though the former is neutral while the latter is acid in character. Moreover since both modifications show acid properties the phenomenon of desmotropism extends also to their salts. L. Knorr [3] closely followed the

[1] Ber., **20**, 2933 (1887).

[2] Ber., **28**, 767 (1895); Annalen der Chemie, **291**, 147 (1896); **312**, 34 (1900).

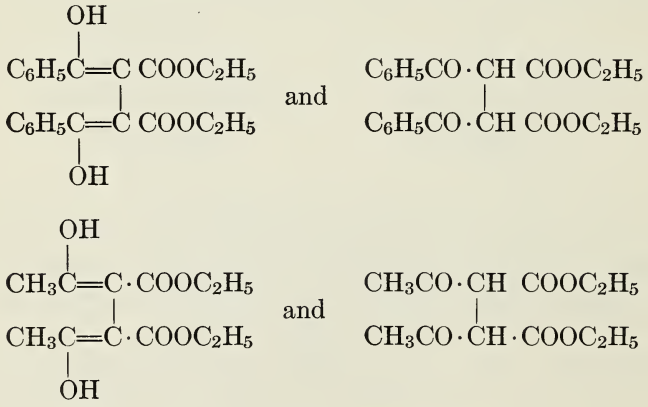
[3] Annalen der Chemie, **293**, 70 (1896); **303**, 133 (1898); **306**, 332 (1899).

publications of Claisen and Wislicenus with several papers which helped to clear up mooted questions in the matter of nomenclature.

Recent work by Michael [1] leads to the conclusion that we have to deal with a more complicated type of isomerism, in the case of ethyl formylphenylacetate, than is expressed structurally by the *enol* and *keto* forms alone. He finds that the β-ester described by Wislicenus as melting at 70° is not a homogeneous substance and is a mixture consisting of 25 per cent of the β-modification melting at 40°, and 75 per cent of a third γ-form to which is assigned a melting point of 100°. According to Michael we are dealing here with α-(liquid), β- and γ-modifications of ethyl formylphenylacetate and all these are monomeric modifications of the *enol*-form. Fuller [2] has made an examination of the behavior of these three forms of this ester and studied their behavior in twenty-four different solvents. His work shows that there is no relation between the dielectric constants of solvents and their isomerizing power. That the α-modification of ethyl formylphenylacetate is to be assigned a ketone structure is supported by the fact that it interacts with phosphorus pentachloride to form a β-dichlor derivative as is expressed in the following equation: [3]

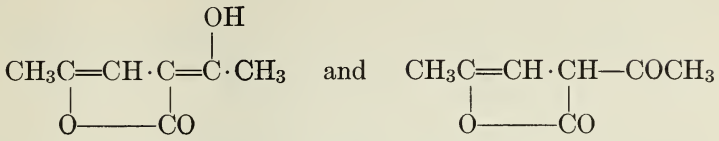
$$OCH \cdot CH(C_6H_5)COOC_2H_5 + PCl_5 \rightarrow Cl_2CH \cdot CH(C_6H_5)COOC_2H_5.$$

Very complicated isomeric relationships have been discovered as the result of the investigation of dibenzoyl and diacetyl succinic esters, since in addition to stereoisomers, structural isomers are formed which are convertible into each other:



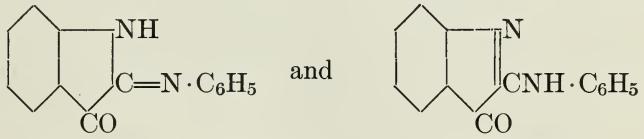
[1] Annalen der Chemie, **391,** 235 (1912).
[2] Annalen der Chemie, **391,** 275 (1912).
[3] Wislicenus, Ber., **51,** 1366 (1918).

Two somewhat similar acetylangelica lactones,



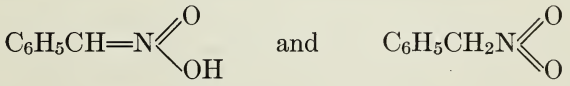
have also been discovered and show the characteristic properties of *enol* and *keto* isomers. Examples of this type of isomerism continue to be discovered, but it will be impossible to refer to more than a few representative types in this text.

Until quite recently desmotropic forms had not been isolated in the isatin series. R. Pummerer,[1] however, claims to have succeeded in separating two isomeric modifications of the anil of isatin, first prepared by Sandmeyer, which he regards as the *lactam* and *lactim* modifications respectively. These desmotropic substances are convertible one into the other and are represented structurally by the following formulas:



Isatin-2-anil Isatin-2-anilide

We are dealing here with a rare case of amidine isomerism rather than one involving true *lactim* and *lactam* modifications (—N=C·OH and NH·CO) and it still remains to be established whether the correct explanation of their desmotropic properties has been given.[2] Desmotropic forms of phenylnitromethane have also been discovered by Hantzsch and Schultze.[3] These substances correspond to the formulas



and will be referred to in detail later.

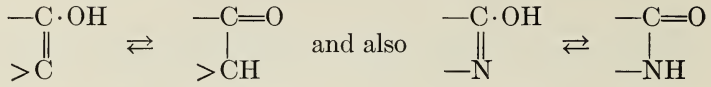
Although a great variety of structural isomers containing the atomic grouping —CO·CH— have been prepared, it has been possible in

[1] Ber., **44**, 338 (1911).

[2] Wheeler and Johnson, Am. Chem. Jour., **31**, 577 (1904). See also Meldola, Eyre, and Lane, Jour. Chem. Soc., **83**, 1185 (1903); **85**, 1592 (1904).

[3] Ber., **29**, 699, 2251 (1896).

almost every instance to convert one modification into the other. It thus happens that although the atomic expressions



were originally used to represent only the end phases of atomic movements operating within one and the same substance, they are now employed to represent different chemical individuals, albeit these must be assumed to be so closely related as to pass readily from one into the other. Baeyer's labile and so-called " pseudoforms " are in terms of this conception actually capable of existence. In order to honor Baeyer, Claisen proposed the substitution of the term " pseudomerism " for tautomerism. Pseudomerism might, be suggested, be either *absolute* or *relative*, the former covering those cases where only one substance is known and the latter, cases where two distinct modifications have been isolated.[1] It has also been suggested by von Pechmann[2] that the expression tautomerism might itself very well be qualified by the adjectives " functional " and " virtual." Functional tautomerism may be used to designate structural differences between two isomeric modifications where these are characterized by marked chemical differences, such as acid and neutral properties, etc. Examples of this are to be found among the various *enol-keto* and *lactim-lactam* modifications which have just been considered. Virtual tautomerism, on the other hand, may be applied to cases where both isomeric forms possess the same constitution, as for example, among the amidine and diazoamido compounds.

Accepted nomenclature at the present time follows neither of the above suggestions but is founded upon proposals made by Knorr to which reference has already been made. The terms desmotropism and tautomerism are both retained, the former being used to designate actual cases of structural isomerism, where one modification has been observed to pass readily into the other as the result of the transposition of the hydrogen atom and a redistribution of affinities within the molecule. For example, the two isomeric modifications of acetyldibenzoyl methane (α and β forms) are desmotropic substances. The term tautomerism, on the other hand, is used to designate cases where the separation of the desmotropic varieties has not actually been realized and where one and the same substance reacts in the sense of two or more structural formulas to give derivatives which are isomeric.[3] Even

[1] Annalen der Chemie, **291,** 46 (1896).

[2] Ber., **28,** 876 (1895).

[3] Tafel, Zeitschr. Elektrochemie, **23,** 60 (1917).

these two terms do not, however, cover all varieties of this class of phenomena.

The relationship represented by the atomic groupings

$$\begin{array}{l} -C-OH \\ \quad \| \\ >C \end{array} \qquad \text{and} \qquad \begin{array}{l} -C=O \\ \quad | \\ >CH \end{array}$$ [1]

is frequently very complicated and the conditions which govern the transformation of one isomer into the other are in many cases not thoroughly understood. Usually one form is much less stable than the other and tends to rearrange even at ordinary temperatures. Thus in the case of the two substances

$$\begin{array}{l} CH_3C\cdot OH \\ \quad \| \\ C(COC_6H_5)_2 \end{array} \qquad \text{and} \qquad \begin{array}{l} C_6H_5C\cdot OH \\ \quad \| \\ C(COC_6H_5)_2 \end{array}$$

the former rearranges into the corresponding *keto* modification only after weeks, while the latter undergoes a corresponding change in the course of a few days. The nature of the substance seems to be a decided factor in transformations of this type. Temperature represents another important factor. Thus:

$$\begin{array}{l} CH_3COH \\ \quad \| \\ C\cdot(COC_6H_5)_2 \end{array}$$

rearranges into the corresponding *keto* form in a few minutes at 90° instead of requiring several weeks as is the case at ordinary temperatures.

Since these and similar rearrangements take place in organic solvents an effort has been made by Claisen, W. Wislicenus, Kurt H. Meyer, L. Knorr and others to follow them quantitatively. This has been possible because of the well-known fact that *enol* modifications of desmotropic substances give color reactions with ferric chloride while the corresponding *keto* forms do not. In the case of ethyl formylphenylacetate Wislicenus made the observation that when solutions of equal volume but of different concentrations were treated with equal small quantities of ferric chloride the intensity of the coloration varied with the concentration of the *enol* form. He also noted that when equal quantities (*a*) of the pure *enol* and (*b*) of the pure *keto* modification were dissolved in equal volumes of alcohol and treated

[1] Wislicenus, "Über Tautomerie." Ahrens' Sammlung chem. u. chem.-techn Vorträge, **2**, 232 (1898).

with ferric chloride, the intensity of coloration became ultimately the same in both cases. This happened, of course, only after the lapse of a period of time since the immediate effect of adding ferric chloride was quite different for the two solutions, *a* becoming at once intensely colored while *b* remained colorless. The conclusion seems obvious that in alcohol solution both phases coexist in a condition of dynamic equilibrium. Equilibrium in such a system depends in general upon the nature of the solvent, the temperature, and the concentration. It has been observed, for example, that *labile* modifications of desmotropic substances may be crystallized unchanged from certain solvents even when the solutions have been warmed, and that under these circumstances and within definite limits of temperature, only one single modification exists. In other solvents both forms coexist at the same temperature and in such cases solution must involve a reversible reaction, as for example,

$$\begin{array}{l} C_6H_5C\cdot OH \\ \quad\| \\ \quad C\cdot(COC_6H_5)_2 \end{array} \rightleftarrows \begin{array}{l} C_6H_5CO \\ \quad| \\ \quad CH(COC_6H_5)_2 \end{array}$$

This finally results in a condition of equilibrium which varies with the temperature. In the case of ethyl formylphenylacetate, increase in concentration favors the *enol* modification.

The application of colorimetric methods [1] to the approximate determination of the relative amounts of the *enol* and *keto* present in various solvents led W. Wislicenus to conclude that at room temperature solutions in methyl alcohol contain only *keto*, in chloroform and in benzene only *enol*, while solutions in ethyl alcohol and ether contain both modifications in equilibrium. These facts suggested the arrangement of various solvents in a series showing the respective influence which each exercised upon the condition of equilibrium in chemical systems of the type:

$$\text{Enol} \rightleftarrows \text{Keto}.$$

Such an arrangement was found to coincide in general with that representing the dissociation constants of these solvents. Since, moreover, dissociation and dielectric constants form parallel series, the relation of equilibrium constants to the latter is obvious. Wislicenus [2] has

[1] Annalen der Chemie, **291**, 179 (1896); K. Meyer, Ber., **44**, 2725; Knorr, ibid., 2772 (1911).

[2] Annalen der Chemie, **379**, 249 (1911).

claimed quite recently that similar relationships exist in the case of such solvents as the indifferent hydrocarbons, chloroform, and alcohols, but no general statement covering the case of all solvents can be made. It has indeed been demonstrated as a result of the investigation of Michael and Hibbert,[1] Dimroth,[2] Kurt H. Meyer[3] and others, that, at least, in certain instances it is quite impossible to establish such relationships.

Michael and Hibbert studied the behavior of dibenzoylmethane and ethyl diacetylsuccinate in solution in a greater number of solvents than had previously been compared. These substances are particularly adapted to this sort of investigation since in both cases the presence of the *enol* and *keto* modifications in the reaction mixture can be readily and almost quantitatively determined. The results obtained by them show that:

1. No simple relationship exists between the dielectric constant, power of dissociation, association factor, heat of vaporization, or tautomerizing energy[4] of organic solvents and their respective rates of isomerization.
2. The rate and the limit of isomerization in organic solvents are independent of each other and the latter does not stand in any simple relationship to the above physical constants.
3. The power of isomerization of an organic solvent is not a constant property but varies with the character of the desmotropic substance. Thus the same solvent may at times enolize and at times ketoize in very different degrees.

Michael and Hibbert not only concluded that no relationship exists between the power of isomerization and the physical constants of organic solvents, but they also regarded it as highly improbable that electrolytic dissociation plays any part in the replacement of hydrogen which is bound to carbon by other radicals. According to Michael, chemical forces are at work, along with other influences, in the process of desmotropic rearrangements in solution. He assumes that complex and unstable addition products are formed, as the result of interaction between the molecules of the solvent and of the solute, and that this involves a constant interchange between the free and bound molecules

[1] Ber., **41**, 1080 (1908).
[2] Annalen der Chemie, **377**, 131 (1910).
[3] Annalen der Chemie, **380**, 226 (1911).
[4] Brühl designates this as "Medialenergie," Zeitschr. physikal. Chemie, **30**, 42 (1899).

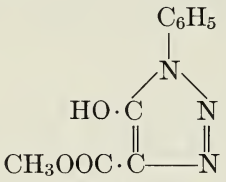
of the solvent. If now the alteration of this complex, as for example, the transformation of

$$[\text{Keto}+\text{solvent}] \rightleftarrows [\text{Enol}+\text{solvent}],$$

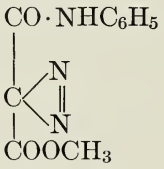
is accompanied by an increase in entropy it follows that solution in this particular solvent will result in isomerization, the degree of isomerization depending upon the relative increase in entropy in any given case. This in turn depends collectively upon the total change suffered by the various physical and chemical forces taking a part in the transformation. It seems very questionable under these circumstances whether a simple relationship between any given physical constant of a solvent and its power of isomerization can ever be established.[1]

O. Dimroth and Kurt H. Meyer have brought forward even more exact evidence to show that the rates of isomerization of organic solvents are in no way paralleled by their respective dielectric constants.[2] While according to these investigations the rate of isomerization does undoubtedly depend upon the nature of the solvent, the relation is far from being as simple as was originally supposed. Not one, but many factors determine the influence which a given solvent will exercise upon the rate of isomerization of desmotropic substances dissolved in it. Among these solubility seems to play an important part.

O. Dimroth [3] made a number of quantitative determinations in different solvents of the rate of the rearrangement expressed below: By com-



Methyl phenyltriazolone carboxylate



Anilide of methyl diazomalonate

paring the solubility number found in each case with the numbers representing the solubility of the acid and neutral forms respectively in the given solvent he discovered that the rate of change of the acid into the neutral ester was influenced by the solubility of the former, viz., the greater the solubility the slower became the rate of isomerization. Solubility and rate of isomerization are, however, only approximately inversely proportional, since other influences which are not as yet understood make themselves felt in this process.

[1] Ber., **41**, 1091 (1908).
[2] Annalen der Chemie, **399**, 91 (1913).
[3] Annalen der Chemie, **377**, 131 (1910).

The effect of the solvent upon the condition of equilibrium must now be considered in detail since in one and the same solvent two reciprocal reactions have frequently been observed. This effect has been analyzed by van't Hoff,[1] who is of the opinion that it is dependent upon two factors. Each of the reciprocal reactions may be supposed to be influenced equally by what may be called the contact action of solvent and solute. The second factor which influences the course of the reaction is, however, specific in character, and depends in some way upon the relative affinity of the solvent for each of the two modifications. The effect of this factor is therefore different in the case of each of the desmotropic forms, and, according to Dimroth, depends upon the relative solubility of the isomers in the given solvent. This relation may be expressed by a modification of van't Hoff's equation:

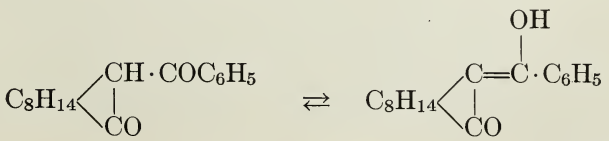
$$\frac{C_A}{C_B} = \frac{L_A}{L_B} \cdot G$$

where C_A and C_B represent the respective concentrations of the desmotropic modifications A and B, and where L_A and L_B represent the solubilities of these substances. G is a constant which depends upon the nature of the solvent and which Dimroth calls the absolute equilibrium constant. Two desmotropic forms are therefore in equilibrium with each other in a given solvent if the ratio of their concentrations equals the ratio of their solubilities multiplied by the constant G.[2] The value of this constant may be calculated if the solubilities of the two substances and the concentration of their equilibrium mixture is known:

$$G = \frac{C_{\text{Enol}}}{C_{\text{Keto}}} \cdot \frac{L_{\text{Keto}}}{L_{\text{Enol}}}$$

Since this value is different for different substances it may be regarded as one of the distinguishing characteristics of any given tautomeric compound.

Dimroth has determined the value of G for the desmotropic modifications of benzoyl camphor



[1] "Vorlesungen über theoret. und physikal. Chemie," 2d edition, Vol. I, pp. 217 and following.

[2] Annalen der Chemie, **377**, 134 (1910).

in solution in a number of different solvents. Both the *enol* and *keto* forms of this substance may be readily obtained in a pure crystalline condition and isomerize slowly enough to make solubility determinations possible. The results of these experiments are given in the following table:

Solvent	$\frac{C_E}{C_K}$	$\frac{L_E}{L_K}$	$G=\frac{C_E}{C_K}\cdot\frac{L_K}{L_E}$
Ether	$\frac{87.2}{12.8}=6.81$	$\frac{12.86}{2.012}=6.39$	1.06
Ethyl acetate	$\frac{66.5}{33.5}=1.98$	$\frac{12.79}{7.05}=1.81$	1.09
Ethyl alcohol	$\frac{62.6}{37.4}=1.67$	$\frac{2.02}{1.31}=1.57$	1.06
Methyl alcohol	$\frac{46.5}{53.5}=0.869$	$\frac{1.49}{1.99}=0.748$	1.15
Acetone	$\frac{46.0}{54.0}=0.852$	$\frac{11.69}{14.53}=0.80$	1.06

It will be observed that the values calculated for G agree closely and fall within the limits of experimental error. The law has, of course, been found to hold in other similar cases.[1]

This work was followed by a systematic investigation of the influence which the substitution of R_1, R_2 and R_3 has upon equilibrium in the system

$$R_1COCH\begin{matrix}R_2\\R_3\end{matrix} \rightleftarrows R_1C(OH)=C\begin{matrix}R_2\\R_3\end{matrix}$$

In developing the problem Kurt H. Meyer[2] studied the condition of equilibrium in the case of ethyl acetoacetate, methyl benzoylacetate and acetylacetone. Fusion mixtures of the desmotropic modifications of these substances were examined and also their solutions in different solvents, and in each instance the percentage of *enol* present in the equilibrium mixture was determined. These results are given in the following table:

[1] Annalen der Chemie, **377**, 134 (1910); **399**, 93 (1913).
[2] Ber., **45**, 2846 (1912); **47**, 826, 832, 837 (1914).

Solvent	Temp. ° C.	Ethyl Acetoacetate	Methyl Benzoylacetate	Acetyl-acetone
Water	0	0.4	0.8	19
Formic acid	20	1.1	2.8	48
Acetic acid	20	5.7	14.0	74
Methyl alcohol	0	6.9	13.4	72
Liquid mixture	20	7.4	16.7	76
Chloroform	20	8.2	15.3	79
Ethyl alcohol	0	12.7	26.0	84
Benzene	20	18.0	31.0	85
Hexane	20	48.0	69.0	92

The figures are significant because they show the same general variation in the case of all three substances. In other words, the different solvents appear to have much the same influence upon the condition of equilibrium in the case of ethyl acetoacetate, methyl benzoylacetate, and acetylacetone, respectively. This is even more apparent when figures representing the equilibrium constants are compared. These values may be readily calculated from those which have just been given and will be found in the following table:

Solvent	Ethyl Acetoacetate	Methyl Benzoylacetate	Acetyl-acetone
Water	0.004	0.008	0.24
Formic acid	0.011	0.028	0.9
Acetic acid	0.061	0.16	2.8
Methyl alcohol	0.074	0.16	2.6
Liquid mixture	0.079	0.20	3.2
Chloroform	0.089	0.19	3.8
Ethyl alcohol	0.15	0.35	5.3
Benzene	0.22	0.45	5.7
Hexane	0.9	2.2	12.0

Very interesting relationships are at once apparent. If the equilibrium constants for the three substances in first one and then another of the given solvents are compared, it will be observed that a rough ratio is maintained. For example, the value for methyl benzoylacetate is approximately 2.2 times as great as that of ethyl acetoacetate in the same solvent, while that of acetylacetone is 30–40 times as great. If, therefore, the equilibrium constant of ethyl acetoacetate in a given solvent is known, that of methyl benzoylacetate in the same solvent

may be roughly calculated by multiplying by 2.2. And, in general, it may be said that if the equilibrium constant of a given desmotropic substance in a given solvent is known, its condition when dissolved in other solvents may be predicted with a certain degree of accuracy.[1]

As a result of his investigation of the equilibrium constants of benzoylcamphor in methyl and ethyl alcohol, O. Dimroth formulated the following rule in regard to equilibrium relationships.[2] If a represents the equilibrium constant for ethyl acetoacetate in a given solvent (I), $n \cdot a$ the equilibrium constant in a second solvent (II) and $m \cdot a$, that in a third (III) and if, further, b and c represent respectively the equilibrium constants of methyl benzoylacetate and acetylacetone in the first solvent, it follows that the equilibrium constants of the last two substances in the second and third solvents will be $n \cdot b$, $m \cdot b$ and $n \cdot c$, $m \cdot c$, respectively.

In other words it is possible to express the general relationships noted in the preceding table in the following way:

Solvent	Ethyl Acetoacetate	Methyl Benzoylacetate	Acetylacetone
I	a	b	c
II	$n \cdot a$	$n \cdot b$	$n \cdot c$
III	$m \cdot a$	$m \cdot b$	$m \cdot c$

where a, b, and c represent the ratios

$$\frac{\text{Concentration of Enol}}{\text{Concentration of Keto}} = \text{Equilibrium constant}$$

in the case of the three substances, respectively. From this it follows that

$$\frac{C_E}{C_K} \text{ in II} = n \cdot \frac{C_E}{C_K} \text{ in I}$$

and that, therefore, the value of n depends not upon the character of R_1, R_2, or R_3 in ethyl acetoacetate, methyl benzoylacetate, and acetylacetone, respectively, but upon the nature of the solvent. This relationship is, of course, not quantitatively exact, but is, nevertheless, approximately correct, and, according to Kurt H. Meyer, demonstrates that the influence of constitution upon the condition of equilibrium in such systems is negligible.

[1] Ber., **45**, 2847 (1912).
[2] Annalen der Chemie, **399**, 96 (1913).

Meyer has found that $G = 0.09$ in the case of ethyl acetoacetate. He also discovered that equilibrium in solutions of ethyl acetoacetate depends upon the concentration. These observations will be referred to again later in the chapter.

L. Knorr has also investigated the effect of heating and of solution upon equilibrium in the case of ethyl diacetylsuccinate. He found that while the *anti* modification, melting at 68°,

$$\begin{array}{l} CH_3CO \cdot CH \cdot COOC_2H_5 \\ \quad\quad\quad\quad | \\ CH_3CO \cdot CH \cdot COOC_2H_5 \end{array}$$

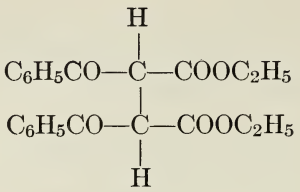
gives no coloration with ferric chloride at ordinary temperatures nor after heating for five minutes at 65°, it nevertheless gives an immediate coloration at its melting point, thus showing that rearrangement of the *keto* to the *enol* modification takes place at this temperature. Similar observations have been made in the case of other desmotropic substances, so that in general it may be said that fusion is frequently accompanied by intramolecular rearrangement. This has suggested to Knorr the possibility that in such cases the phenomena of fusion (and therefore the melting point) are actually rearrangement phenomena and involve chemical as well as physical changes.

In still other instances rearrangement has been observed to begin at temperatures above the melting point. This would seem to indicate that in such cases one of the desmotropic modifications is stable at low temperatures and that increase in temperature leads to a point at which it ceases to be stable and tends to rearrange wholly or in part into its corresponding isomer. The temperatures at which desmotropic substances cease to be stable are referred to by Knorr as the "limits of stability."[1] These limits may or may not correspond to the melting points. Indeed observation shows that they vary considerably. Thus in the case of the β- and γ-diacetyl succinic esters, for example, the limits of stability correspond to the melting points of the substances, while in the case of the corresponding β-dibenzoyl succinic ester,

$$\begin{array}{l} \quad\quad\quad H \\ \quad\quad\quad | \\ C_6H_5OOC—C—COOC_2H_5 \\ \quad\quad\quad | \\ H_5C_2OOC—C—COC_6H_5 \\ \quad\quad\quad | \\ \quad\quad\quad H \end{array}$$

[1] Annalen der Chemie, **293**, 88 (1896).

there is no coloration with ferric chloride at 128°–130° which represents the melting point of the substance, although brief heating at 170° produces enolization. On the other hand γ-ethyl dibenzoyl succinate

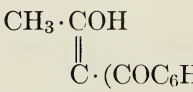


which melts at 75°, shows a tendency to enolize after short heating at 150°–160°. The ketone ester obtained by condensation of mesityloxide with diethyl oxalate

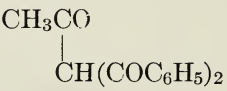
$$(CH_3)_2C=CH\cdot COCH_2COCOOC_2H_5$$

which melts at 59°–60°, isomerizes only at 130°.

Knorr assumes that in these and similar cases enolization begins at the melting point of the substances, although this cannot be demonstrated experimentally. He explained the equilibrium relationships which have been observed in the case of Claisen's desmotropes by supposing that the limits of stability of the *enol* form,



which melts at 101°–102°, are 80°–90°, while those of the *keto* form,

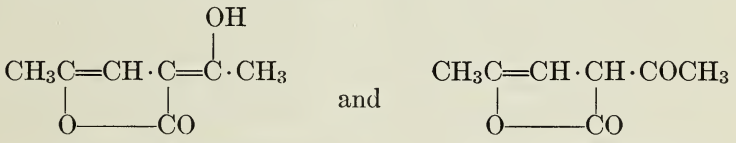


which melts at 107°–110°, are about 110°. On these assumptions it follows that below 90° both desmotropic modifications may be regarded as stable and capable of existing side by side; between 90° and 110° the *enol* form is labile, the *keto* stable; and above 110° both forms are labile. In this last case neither form is capable of maintaining an independent existence since each tends to pass into the other and a condition of equilibrium between the two is established which is analogous in character to that which is observed in connection with solution phenomena.

Equilibrium mixtures, the composition of which varies with changes in temperature, are referred to by Knorr as "allelotropic mixtures." In other words, an allelotropic mixture is a homogeneous mixture of two desmotropic substances which mutually rearrange each into the other. From a consideration of energy relations it is obvious that allelotropism is possible only in the case of liquids or of dissolved substances.[1]

The phenomena of allelotropism may be readily interpreted in terms of C. Laar's hypothesis. Assuming that both *enol* and *keto* modifications are continually changing one into the other and that in a given interval of time the amounts of each which undergo change are equal, it follows that a condition of equilibrium must result from the fusion as well as from the solution of the substance. Changes in temperature will bring about conditions which favor one form at the expense of the other so that ultimately a temperature must be reached at which one form will so predominate in the mixture as to make the presence of the other negligible and even incapable of experimental demonstration. Baeyer's term "pseudo-form" is employed by Knorr to denote this almost completely eclipsed modification. According to this conception the pseudo-form represents the limit of allelotropism.

Acetylangelica lactone exists, for example, in two distinct forms,



Enol (melting at 63°) Keto (melting at 177-180°)

These two forms readily pass into each other and therefore represent a typical case of desmotropism. Each is partially isomerized on solution in hot alcohol, benzene, acetone, and ethyl acetate, and the resulting mixture is found to contain both modifications in proportions which are constant for any given temperature, but which vary for different temperatures. These solutions obviously contain allelotropic mixtures of the two acetylangelica lactones. Such mixtures may also be obtained by heating the *keto*-modification at temperatures above its melting point. If, however, the ketone is distilled under diminished pressure it practically disappears and must, therefore, be regarded as having passed into the *pseudoform* of acetylangelica-lactone. To recapitulate:

1. Desmotropism may be regarded as a special form of structural isomerism where the difference in the properties of any two substances depend upon a difference in the relative position of a hydrogen atom in

[1] Compare Schaum, Ber., **31**, 1964 (1898); also "Die Arten der Isomerie," Habilitationsschrift Marburg.

the molecule. It is observed in the case of substances in the solid state. Thus the isomeric triacylmethanes,

$$\begin{array}{l} CH_3C\cdot OH \\ \| \\ C\cdot(COC_6H_5)_2 \end{array} \qquad \text{and} \qquad \begin{array}{l} CH_3CO \\ | \\ CH\cdot(COC_6H_5)_2 \end{array}$$

may exist independently of each other below, but never above 80°. The fact that one modification does in time pass over into the other is explained by Knorr as due to the presence of minute traces of some solvent.[1]

2. Tautomerism is the phenomenon observed when one and the same substance reacts in two senses—viz., as *enol* and *keto*. In such cases, however, the two forms have never been separated. The phenomenon occurs in connection with substances in both the solid and the liquid state. If the substance is a solid, even though it reacts in two senses, it itself must be regarded as having a perfectly definite structure and as representing either the *enol* or *keto* modification. This is in agreement with Baeyer's conception, but in contradiction to that of C. Laar. If the tautomeric substance is a liquid it must in general be regarded as representing an allelotropic mixture. Such a mixture may be of two types: (*a*) where both *enol* and *keto* modifications are present and where their presence may be experimentally demonstrated; (*b*) where the conditions of temperature, etc., favor one form to the exclusion of the other, so that the presence of only one of the two possible modifications can be experimentally demonstrated. Such a condition is referred to as pseudomerism and represents the extreme limit of allelotropism.

Mixtures of solid desmotropic substances must not be confused with allelotropic mixtures. Examples of the latter class are recorded in the following table:

Acetyl benzoylmethane Mesityloxide oxalic ester Tribenzoylmethane *p*-Brombenzoyl-dibenzoylmethane Ethyl diacetylsuccinate Ethyl dibenzoylsuccinate Ethyl acetoacetate, etc.	When present in fluid condition and in solution.

To this list may be added ethyl formylphenylacetate, if, according to Knorr, it may be regarded as a mixture consisting of large quantities of the α and small quantities of the β form in equilibrium with each other.[2]

[1] Annalen der Chemie, **313**, 147 (1900).

[2] Annalen der Chemie, **396**, 340 (1899); **313**, 141 (1900).

Pseudomerism is limited to cases of tautomerism where only one form, whether *enol* or *keto*, may be experimentally demonstrated. Illustrations are to be found in benzoyl diacetyl methane, *p*-brom benzoyl acetone and the anhydride of diacetyl succinic acid and its ester. These substances are known only in the *enol* form. The corresponding ketones have not been isolated in solid condition and do not appear to be formed when the substances are either fused or dissolved.

The quantitative determination of the relative amounts of the *enol* and *keto* modifications which are present in allelotropic mixtures is naturally of the greatest importance. This task is the more complicated and difficult because of the fact that the equilibrium relationships in such systems are extremely sensitive to changes in temperature and to the action of different solvents, catalytic agents, etc. If, for example, the *enol* modification reacts with ferric chloride, an iron enolate, $FeCl_2 \cdot R$ (where R represents the *enol* residue) is formed and at the same time a molecule of hydrochloric acid is set free. This acid in concentrated form can materially alter the condition of equilibrium even in the very short space of time required for the color change. It has also been discovered that ferric chloride itself acts directly as a catalyst and in the case of ethyl acetoacetate, for example, brings about the enolization of the *keto* form. In this particular case the quantity of *enol* which forms depends upon the quantity of ferric chloride which is used, but is not, however, directly proportional to it.[1] These errors in experimentation have been reduced to a minimum by employing various artifices and in particular by working at low temperatures. L. Knorr [2], in co-operation with H. Schubert, has recently succeeded in perfecting a colorimetric method for the quantitative determination of the *enol* modification present in allelotropic mixtures, to which reference will be made again later in the text.

Kurt H. Meyer [3] has developed another quantitative method which will be referred to again in connection with the more detailed consideration of ethyl acetoacetate. It is founded upon the observation that *enol* forms in contrast to *keto* react readily with bromine. In its typical form this reaction involves the direct addition of bromine to the double bonds of the carbon atoms, and of course presupposes that bromine does not react with other groups present in the molecule. There are naturally many sources of error in the application of this reaction, especially since bromine on mere contact acts as a catalyst and tends to bring about rearrangements. In spite of these difficulties, however,

[1] K. Meyer, Ber., **44**, 2726 (1911).
[2] Ber., **44**, 2772 (1911).
[3] Annalen der Chemie, **380**, 212 (1911).

Meyer, in co-operation with P. Kappelmeier,[1] succeeded by the use of various artifices in so perfecting the method as to have it compare favorably with the ordinary analytical methods in accuracy.

It may be said in general that the application of many physical methods involves fewer possibilities of experimental error than is the case with chemical methods. This is especially true if in the process the substances themselves are subjected to no change. The results which are obtained by the use of physical methods are, however, valuable only in so far as they may serve for comparisons between the substance in question and other very closely related substances whose exact chemical character has been accurately determined. The reliability of the conclusions which are drawn from such data depends naturally upon whether sufficient material is available for comparison. The methods of molecular refraction and rotation, Drude's method of electrical oscillations of definite period, together with many others, have been of great service in the solution of the problems of structural chemistry.[2]

As has already been stated, solvents are instrumental, along with other agencies, in inducing rearrangements in the case of tautomeric and desmotropic substances. Rules governing transformations of this type were early recognized by Wislicenus as a result of his researches on ethyl formylacetate, and these were confirmed in the main by later investigations. They have been formulated by H. Stobbe[3] as follows:

Solvents may be divided in general into two groups according to their ability to isomerize tautomeric substances under constant conditions of temperature. To the first group belong water, alcohol, and other oxygen compounds, or, in general, those solvents which are characterized by a tendency to dissociate. Such solvents are effective both in starting and in accelerating the enolization of neutral *keto* forms and the ketonization of acid *enol* forms. In so far as experimental evidence goes they do not seem to combine with the dissolved substance, and their action must, therefore, be regarded as catalytic. To the second group belong chloroform, benzene, and other substances which contain no oxygen and whose power of dissociation and isomerization is very weak. Such solvents not only do not actively accelerate reversible reactions of the type under consideration, but in certain instances they may even serve as media for conserving the transitory

[1] Ber., **44**, 2718 (1911).

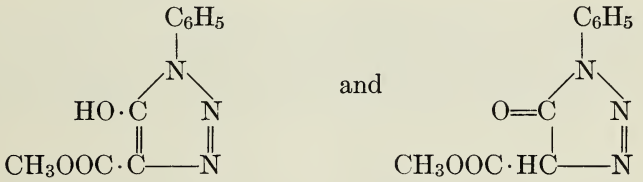
[2] For a summary of these different methods consult Wislicenus' monograph entitled "Über Tautomerie" and also Annalen der Chemie, **291**, 176 and 217 (1896), Zeitschr. physikal. Chemie, **30**, 1 (1899); Knorr, Annalen der Chemie, **306**, 342 (1899).

[3] Annalen der Chemie, **326**, 359 and following (1903).

condition of a tautomeric substance. At times they may even hinder isomerization and may, therefore, perhaps be regarded as catalysts in a negative sense.

The fact that tautomeric substances isomerize so readily on solution and upon fusion is particularly remarkable and characteristic and at once recalls C. Laar's oscillation hypothesis. The results of experiment show that mutual rearrangements take place more or less readily and finally result in a condition of equilibrium. It is thus possible to consider the process from the standpoint of the kinetic theory of gases and to suppose the existence of a condition of dynamic equilibrium whereby in a given interval of time the same number of molecules undergo transformation in one direction as in the other.

The rate of this rearrangement was originally followed in a qualitative sense only, but in 1904 O. Dimroth [1] made the first quantitative measurements. He had discovered two triazol derivatives as the result of condensing diazobenzene imides with diethyl malonate and had interpreted the phenomena by supposing that the two substances were desmotropic modifications corresponding to cyclic formulas:

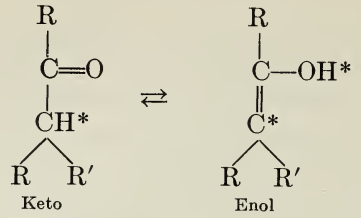


Of these the *keto* form was found to be absolutely neutral in character while the *enol* was sufficiently acidic to decompose a solution of potassium iodide, freeing exactly one atomic equivalent of iodine for every equivalent of acid. Since the methods involved the use of neutral reagents, all disturbing influences were eliminated and Dimroth was able to determine quantitatively the amount of *enol* present at any moment during the course of the reaction. He thus succeeded in applying the laws governing the rates of reaction to this particular transformation, and discovered that it belongs to the general class of monomolecular reactions.

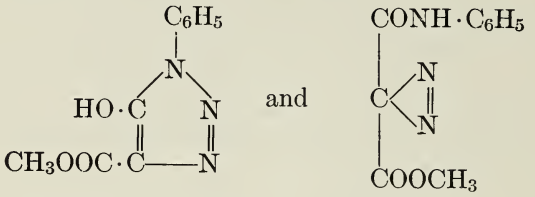
Dimroth then showed that it was possible on the basis of the kinetic molecular hypothesis to calculate from the constants for the rates of reaction the interval of time necessary for one molecule to rearrange into *enol* and then back again into the *keto* form, or, in other words

[1] Annalen der Chemie, **335**, 1 (1904); **338**, 143 (1905).

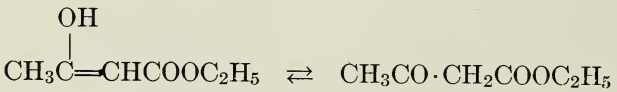
the interval of time necessary for one complete oscillation of a hydrogen atom in the sense of Laar's hypothesis, viz.:



Although Dimroth discovered later that his two triazol derivatives could not be interpreted as desmotropic modifications, but that they must be regarded as the structural isomers,



his deductions have, nevertheless, been applied recently to a solution of the problem involved in the chemistry of ethyl acetoacetate. This substance consists of an equilibrium mixture of *enol* and *keto* forms:



Each of these substances has recently been obtained in pure or almost pure condition, and it has been observed that if either is allowed to remain for some time at room temperature it rearranges—the *enol* into the *keto* and vice versa. The final product consists in each case of a mixture composed, according to Kurt H. Meyer,[1] of 7.4 per cent *enol* and 92.6 per cent *keto*, or, according to L. Knorr, of 2 per cent *enol* and 98 per cent *keto*. This phenomenon is explained on the basis of the kinetic molecular hypothesis by supposing that the two forms are constantly in a condition of dynamic equilibrium with reference to each other The fact that the amount of *keto* present in the mixture after equilibrium has been reached is proportionally greater than the amount of *enol*, serves to show that ketonization proceeds much more rapidly than enolization. These rates of transformation have now been determined very exactly and under the most varied

[1] Ber., **44**, 2720 (1911); also **47**, 837 (1914).

conditions[1] and it has been found that in alcohol solution and at zero degrees, for example, the volocity constants are, respectively:

$$\text{Enol} \rightarrow \text{Keto}, \; K_1 = 0.077$$
$$\text{Keto} \rightarrow \text{Enol}, \; K_2 = 0.0105$$

These figures show that under these conditions 0.077 or 7.7 per cent of the *enol* present is transformed into *keto* and 0.0105 or 1.05 per cent *keto* is changed into *enol*. In other words, in any given interval of time, $\frac{100}{7}$, or, roughly, 13 molecules of β-hydroxycrotonic ester are isomerized to ethyl acetoacetate, while $\frac{100}{1.05}$, or, roughly, 95 molecules of ethyl acetoacetate are isomerized to β-hydroxycrotonic ester. Every 95 minutes a single molecule of ketone has the chance to become *enol*, and every 13 minutes a single molecule of *enol* has the chance to become *keto*. Thus 108 minutes are required for the following series of transformations:

$$\text{Keto} \rightarrow \text{Enol} \rightarrow \text{Keto}$$

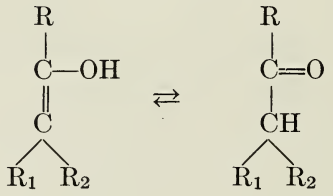
and this interval of time represents the period of oscillation of the hydrogen atom. In aqueous solution it has been found that the period of oscillation requires 100 minutes; in liquid ester, 2400 minutes or 17 days.

These figures are in contradiction to our conception of intramolecular atomic movements in the sense of the kinetic theory of gases. They must, therefore, be regarded as representing the periods of extreme deviation from the regular course of the atom. In the words of O. Dimroth:[2] " Just as the path or course of individual molecules is supposed, according to the kinetic theory of gases, to vary greatly during successive intervals of time and to show frequently considerable divergence from the average, so the course of individual atoms only approximates a mean. In the case of tautomeric substances, for example, it may be assumed that the range of the hydrogen atom, and therefore the extreme distance which may separate it from its point of union with carbon and oxygen, respectively, may vary greatly in different molecules. The average range is probably in most cases less than the distance between a carbon and an oxygen atom, but may at times be imagined as equal to it." When the latter condition exists, rearrangements from *enol* to *keto*, or vice versa, will take place. In the instance just cited it occurs in alcohol solutions every 13 and every 95 minutes, respectively.

[1] Annalen der Chemie, **380**, 239 (1911).
[2] Annalen der Chemie, **335**, 17–18 (1904).

Since this tendency for rearrangement is recognized as a characteristic property of all tautomeric and desmotropic substances, these reactions should be followed by means of velocity determinations wherever this is possible. Such methods should also be improved. To quote Dimroth [1] again: "an exact description of a desmotropic substance requires a knowledge, not only of the quantities in which two isomers are present, but of the time which is required in order to establish a condition of equilibrium between them." Dimroth is himself convinced that the innumerable variations observed in connection with phenomena of this kind depend upon enormous fluctuations in velocity values. If, for example, one modification rearranges much more rapidly than the other the reverse reaction will become negligible, equilibrium will disappear and the phenomenon will assume the aspect of pseudomerism. If, however, both modifications possess very great and approximately equal isomerization velocities a condition will arise which corresponds to that which Laar's oscillation hypothesis seeks to explain. If, finally, the isomerization velocities are small a condition of apparent stability will result and the phenomenon will assume the aspect of desmotropism.[2]

The question as to the cause and mechanism of tautomeric rearrangements has been answered in a variety of ways.[3] The simplest explanation is one which assumes that the whole molecule is changed because of a change in the relative position of a hydrogen atom;



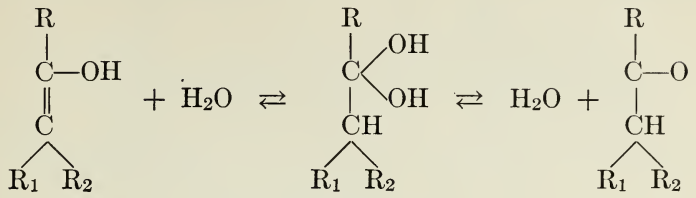
In this case the migration of the hydrogen atom is supposed to have nothing to do with the phenomenon of electrolytic dissociation and the reaction is assumed to be mono-molecular. Another explanation which has been quite widely accepted by workers in this field supposes that

[1] Annalen der Chemie, **335**, 5 (1904).

[2] Annalen der Chemie, **335**, 5–6 (1904).

[3] Ber., **28**, 708 (1895); **30**, 2388 (1897); Annalen der Chemie, **293**, 34, 100 (1896); **306**, 342 (1899); **291**, 176 (1896); Ahrens' Samml. Chem. u. chem. techn. Vorträge, **2**, 230 (1898); Ber., **32**, 2326 (1899); Zeitschr. physikal. Chemie, **30**, 38 (1899); Jour. Chem. Soc., **81**, 1508 (1902); **85**, 48 (1904); Annalen der Chemie, **335**, 1 (1904); **338**, 143 (1905); Zeitschr. Elektrochemie, **11**, 137 (1905); Ber., **41**, 1080 (1908).

rearrangement is due to the alternate addition and splitting off of a molecule of water according to the scheme:

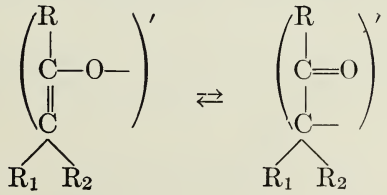


This should, of course, be capable of experimental verification.

A third explanation supposes that rearrangements of tautomeric substances are due to electrolytic dissociation. The fact that tautomeric substances are frequently formed when solutions of sodium salts react with alkyl halides led H. Goldschmidt in 1890 to suppose that in such cases rearrangement is directly due to the influence of free ions.[1] Immediately after this P. Walden [2] and Mullikan [3] discovered a number of tautomeric substances which acted as electrolytes either in their free state or in the form of their salts, and in 1895 Knorr supplied additional evidence along the same line as a result of his researches on phenylmethylpyrazolones. Tautomerism in the case of these substances was, in his opinion, due to the electrolytic dissociation of hydrogen.

Such a conception has the advantage of accounting for the remarkable ease with which tautomeric rearrangements take place. The mechanism of the change has been explained in a number of different ways:

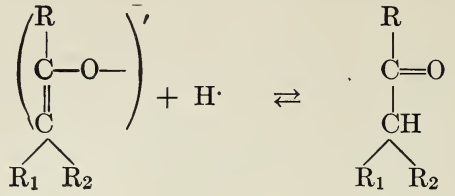
I. The hydrogen ions may be assumed to take no part in the reaction which involves a redistribution of affinity inside the anions. This explanation applies only where the rate of rearrangement is proportional to the concentration of the anions.



II. The hydrogen ions may be regarded as taking part in the change in either one of two ways:

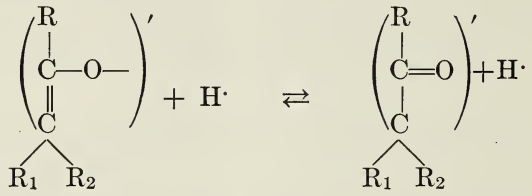
[1] Ber., **23**, 257 (1890).
[2] Ber., **24**, 2025 (1891).
[3] Am. Chem. Jour., **15**, 523 (1893).

(*a*) By reaction with anions to form undissociated molecules of ketonic ester:[1]



Such an explanation applies only in cases where the electrolytic dissociation of an electrically neutral body takes place and does not hold in the case of alletropic mixtures since the rearrangement of desmotropes is reciprocal and the *keto* modifications are neutral bodies.

(*b*) By reaction as catalysts,[2] and in this way inducing rearrangement from enolions to ketonions and vice versa:



Such an interpretation holds only in cases where the reaction has been shown to be bimolecular.

In conclusion it may be said that any explanation as to the cause and mechanism of tautomeric rearrangements must in any particular instance depend finally upon the experimental data. In order to understand better what this implies it may be well to consider briefly the individual case of ethyl acetoacetate since this is one of the most interesting as well as one of the most widely investigated of all tautomeric substances.

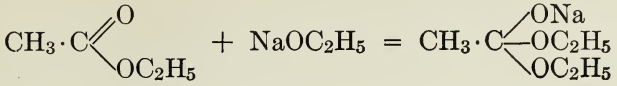
This β-ketone ester was discovered by Geuther, who prepared it by interaction of ethyl acetate with sodium, and gave it the formula

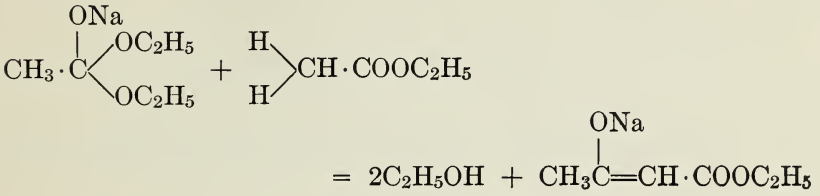
$$CH_3 \cdot \overset{\overset{OH}{|}}{C}{=}CH \cdot COOC_2H_5$$

in order to account for the fact that it is capable of forming a metallic derivative with sodium. Later it was prepared by Claisen from ethyl

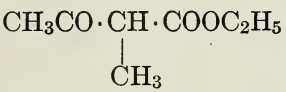
[1] Jour. Chem. Soc., **81**, 1509 (1902); Ber., **32**, 2329 (1899).
[2] Schaum, Ber., **31**, 1964 (1898).

acetate by the action of sodium ethylate. This reaction was interpreted in the sense of Geuther's formula by means of the following scheme:



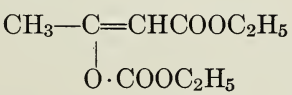


The hydroxycrotonic acid formula failed, however, to explain many of the reactions of this interesting substance. For example, methyl iodide reacts with the sodium salt of ethyl acetoacetate to give a product in which the methyl group would seem to be in union with carbon and not with oxygen as was to be expected. All of the reactions of this substance point in fact to the formula



and it must, therefore, be regarded as a derivative of a true ketone, $CH_3COCH_2COOC_2H_5$. Indeed at this time so many of the reactions of ethyl acetoacetate were found to be in harmony with the above formula that not only did it displace the original hydroxycrotonic acid formula, but even the sodium derivative of ethyl acetoacetate came to be written as $CH_3CO \cdot CH(Na) \cdot COOC_2H_5$.

In the course of time, however, an increasing number of substances were discovered which corresponded to Geuther's formula. Thus the main product of the reaction between ethyl chloroformate and the sodium salt of ethyl acetoacetate is



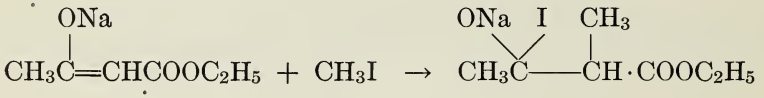
although the isomeric acetylmalonic ester

$$CH_3CO \cdot CH(COOC_2H_5)_2$$

is also formed in small quantities. This reaction definitely proves that ethyl acetoacetate is capable of reacting in the sense of two different

formulas, and that it is therefore a tautomeric substance. The question as to the mechanism of these reactions still remains to be answered. Is the hydrogen atom actually in such a state of continual vibration in the molecule that the substance is at any moment capable of reacting in two ways or has the substance a fixed and definite structure which suffers isomerization prior to the formation of derivatives possessing a different structure?

On the basis of the latter assumption it was possible to support anew the hydroxycrotonic acid formula for ethyl acetoacetate. The formation of alkylated derivatives, for example, has been explained by Nef on the assumption that the alkyl halide adds directly to the ethylene carbon atoms,



and that the hypothetical addition product then decomposes immediately to give sodium iodide and the carbon substituted ester $CH_3CO \cdot CH(CH_3)COOC_2H_5$. The objection to this interpretation as to the course of the reaction is to be found in the fact that no addition products of this type have as yet been isolated. Although it was thought quite recently that substances of this type had finally been discovered it was proved that colloidal sodium halide combinations had been mistaken for them.[1]

In 1900 Claisen[2] succeeded in regulating the conditions governing the reaction between acid chlorides and ethyl acetoacetate so as to obtain at will either one of two classes of derivatives—viz., those in which the acyl group is in union with oxygen or carbon, respectively. Acyl derivatives of the hydroxycrotonic acid type were obtained almost exclusively when ethyl acetoacetate was treated with acid chlorides in the presence of pyridine, while substitutions of the acyl group on the methylene carbon occurred when sodium alcoholate was used as a condensing agent. It was discovered further that derivatives of the first class could be transformed into the second by warming with potassium carbonate or, better, with the potassium salt of ethyl acetoacetate.

As a result of these investigations it seems probable that derivatives of the hydroxycrotonic acid type form the primary products in the alkylation of ethyl acetoacetate, and that these then suffer a secondary

[1] Ber., **38**, 3217 (1905); **39**, 1436 (1906).
[2] Ber., **33**, 1242, 3778 (1900).

rearrangement under the influence of the sodium salt of ethyl acetoacetate as is expressed by the following equation:

$$CH_3C(ONa)=CHCOOC_2H_5 + C_2H_5I \rightarrow CH_3C(OC_2H_5)=CHCOOC_2H_5 + NaI$$

$$CH_3C(OC_2H_5)=CHCOOC_2H_5 \rightarrow CH_3COCH(C_2H_5)COOC_2H_5$$ [1]

I II

This explanation, however, also lacks complete experimental demonstration, for while Claisen has succeeded in preparing β-ethoxycrotonic ester, he never was able to transform either it or the β-methoxy derivative

$$CH_3C(OCH_3)=CHCOOC_2H_5$$

into the corresponding α-ethyl and α-methyl acetoacetates.

The general status of the whole question may be summed up by saying that the sodium derivative of ethyl acetoacetate is commonly supposed to have the formula

$$CH_3C(ONa)=CHCOOC_2H_5$$

while the β-ketone ester itself is regarded as an equilibrium mixture of both modifications (*enol* and *keto*)

$$CH_3C(OH)=CHCOOC_2H_5 \rightleftarrows CH_3CO\cdot CH_2COOC_2H_5$$

The latter fact has been demonstrated through the researches of Stobbe [2] and Hantzsch [3] who have recently succeeded in resolving ethyl acetoacetate into its desmotropic forms. Both *keto* and *enol* modifications have also been separated in pure condition from the equilibrium ester as a result of the efforts of Knorr [4] in conjunction with his students, O. Rothe and H. Averbeck. The *keto* modification may be obtained by extracting ordinary ethyl acetoacetate with ether, alcohol, hexane, and other solvents cooled at −78° when the pure ester separates in

[1] Ber., **45**, 3157 (1912).
[2] Annalen der Chemie, **352**, 132 (1907).
[3] Ber., **43**, 3049 (1910); **44**, 1773 (1911).
[4] Ber., **44**, 1147 (1911).

crystalline form on evaporation of the solvent. The *enol* modification, on the other hand, may be obtained by decomposing the sodium salt of ethyl acetoacetate at −78° with dry hydrochloric acid gas. The properties of the pure substances and of their equilibrium mixture are shown in the following table:

Ethyl Acetoacetate $CH_3COCH_2COOC_2H_5$	Ethyl β-Hydroxycrotonate $CH_3C(OH)=CH\cdot COOC_2H_3$	Equilibrium Ester (Enol and Keto)
Long, colorless needles melting at −39°. Crystallizes from concentrated solutions of ether or ethyl alcohol at −78°.	Colorless oil at −78°, when cooled with liquid air solidifies to a glassy mass which soon becomes crystalline.	Liquid.
Distills between 40°–41° at 2 mm. pressure.	Distills unchanged at 33° in a strong vacuum if small quantities are used.	Distills between 39° and 40° at 2 mm. pressure.
$n_D^{10}=1.4225$	$n_D^{10}=1.4480$ $d_4^{10}=1.0119$	$n_D^{10}=1.423-1.4232$
Does not react at once with $FeCl_3$ at −40°; but will react slowly, due to the catalytic action of $FeCl_3$.	Reacts instantly with $FeCl_3$ even at −78°.	
Does not react instantly with bromine.	Reacts instantly with bromine.	
Unchanged at −78° for long periods of time if no catalytic agent is present.	Unchanged at −78° for long periods of time if no catalytic agent is present.	
Rearranges to form the equilibrium ester at room temperature in the course of weeks or even months.	Rearranges to form the equilibrium ester at room temperature in from 10 to 14 days.	

The *keto* and *enol* modifications of ethyl acetoacetate also differ considerably in their respective indices of refraction for sodium light. Knorr, with the assistance of his students, has determined the indices of refraction in the case of mixtures containing known quantities of the

two forms and has obtained the following values for wave length *D* at 10° C.

Per Cent Enol	n_D^{10}	Per Cent Enol	n_D^{10}
0	1.4225	50	1.4352
2	1.4230	75	1.4417
25	1.4287	100	1.4480

Since the index of refraction of ordinary ethyl acetoacetate has been found to be equal to 1.423 under these conditions, it would seem to follow that this substance may definitely be regarded as an allelotropic mixture consisting of about 2 per cent of the *enol* and 98 per cent of the *keto* modification.

Working along somewhat different lines Kurt H. Meyer [1] has obtained values which seem to indicate the presence of a rather higher per cent of *enol* in the equilibrium mixtures than the 2 per cent referred to above. Meyer's method was based upon the fact that in alcohol solution the *enol* modification reacts instantly with bromine while the *keto* form does not. It is thus possible to determine the amount of *enol* present in a given equilibrium mixture by direct titration with bromine. Certain difficulties had to be overcome, however, in the working out of this method since it was necessary to obviate the possibility of any change in the condition of equilibrium during the process of titration if the results were to prove reliable.

It was known, for example, that the mere act of dissolving the ester might produce change in the composition of the mixture, since solution has frequently been shown to favor the formation of one desmotropic modification at the expense of the other. The presence of bromine in excess might also serve to bring about such a change, for this reagent has been observed to function as a catalyst in certain instances and to induce isomerization in a given direction. While these and other obvious sources of error undoubtedly exist, Meyer and Kappelmeier were, nevertheless, able,—by working at low temperatures and by avoiding the presence of an excess of bromine,—to reduce these errors to a minimum and thus to develop the method to a very high degree of accuracy. Their results show that at ordinary temperatures the so-called " equilibrium ester " contains 7.4 per cent of the *enol* modification. The difference between these figures and those of Knorr has

[1] Annalen der Chemie, **380**, 220 (1911); Ber., **44**, 2718 (1911).

not as yet been explained.[1] Nevertheless the two experiments taken together firmly establish the fact that ordinary ethyl acetoacetate is indeed an allelotropic mixture consisting of a relatively large quantity of the *keto* and a small quantity of the *enol* modification.

The condition of equilibrium in ordinary liquid ethyl acetoacetate was only very slightly changed by heating at its boiling point.[2] It showed in two separate titrations, 7.22 and 6.92 per cent of *enol*. Freshly distilled ethyl acetoacetate, on the other hand, contains 20–25 per cent of *enol*, but reverts on long standing to the ordinary equilibrium mixture. These observations are in general agreement with those of Schaum and Traube, who have noted that freshly distilled ethyl acetoacetate possesses a different specific gravity and also a different viscosity from that of ordinary ethyl acetoacetate.

Velocity determinations show that ketonization takes place much more readily than enolization. As the result of a series of titrations Meyer found that the constants K_1 and K_2 are equal, respectively, to 0.00055 and 0.000046 and it has since been calculated that the period required for a complete oscillation from *keto* → *enol* → *keto* equals approximately 17 days.[3] In visualizing this process according to the terms of the kinetic theory, the hydrogen atom must be imagined as in constant and rapid motion. The average distance traveled in any single oscillation is not, however, sufficient to bring the hydrogen outside the sphere of influence of the atom (oxygen or carbon) with which it is in union and does not, therefore, result in any change in the distribution of affinity within the molecule. Since, however, individual oscillations must be supposed to vary considerably in range, it may happen that once in every 17 days the velocity of the hydrogen will prove sufficient to carry it beyond the sphere of its own atom and within the radius of attraction of the adjacent (carbon or oxygen) atom. Under these conditions an exchange of valencies would result.

The period required for a complete oscillation from *keto* → *enol* → *keto* is influenced in different degrees by different solvents. Thus in aqueous solution it equals 100 minutes and in alcohol 108 minutes. Catalytic agents have a tendency to shorten this period.

While equilibrium mixtures of ethyl acetoacetate have been found to vary considerably under different conditions, equilibrium may in general be said to depend upon the nature of the solvent, the degree of solubility in the solvent, the temperature, and the relative concentration of both forms in the solution.

[1] Meyer's work has recently been repeated and verified. See Ber., **47**, 837 (1914).
[2] Compare Ber., **44**, 2732 (1911).
[3] Annalen der Chemie, **380**, 235 (1911); compare Knorr, Ber., **44**, 1147 (1911).

The per cent of *enol* present in various solvents at a temperature of 10° C. has been determined by Knorr, Rothe, and Averbeck [1] by means of optical methods. Their results are given in the following table:

Solvent	Percentage concentration of the solution	Percentage of *enol*
Ethyl ether	30	11.0
Carbon bisulphide	30	25.0
Chloroform	50	2.0
Petroleum ether	3	27.5
Hexane	3	31.0

The influence of concentration upon the equilibrium of such systems has been investigated by Meyer and Kappelmeier, who have found that within the limits which may be accurately studied by titration methods, dilution seems to favor the formation of the *enol* modification.[2] The results obtained with solutions of ethyl acetoacetate in absolute ethyl alcohol are recorded in the following table:

Percentage of ester in solution	Percentage of *enol* form	Percentage of ester in solution	Percentage of *enol* form
65	7.8	11.0	11.6
57	8.1	5.6	12.5
34	8.7	2.2	12.7
25	10.2	0.8	13.2
19	10.8	....	....

Changes in the condition of equilibrium due to substitutions in the ethyl acetoacetate molecule have been investigated by Knorr and co-workers and their results show that while the ethyl ester contains 7.4 per cent *enol* under ordinary conditions, the corresponding methyl ester contains only 4 per cent. Ethyl benzoylacetate has also been studied by Knorr [3] and Meyer,[4] both of whom have succeeded in separat-

[1] Compare K. Meyer, Annalen der Chemie, **380**, 226 (1911).

[2] For solution in benzene, carbon bisulphide, and hexane see Ber., **44**, 2723 (1911); also see Annalen der Chemie, **380**, 231 (1911).

[3] Ber., **44**, 2767 (1911).

[4] Ber., **44**, 2729 (1911).

ing the *enol* modification in pure condition. This substance is described as a white solid which melts at 41° C. The ester in common use consists of an allelotropic mixture which contains a relatively smaller percentage of the *enol* than of the *keto* modification. In the case of the methyl ester the *enol* present equals 16.7, and in the case of the ethyl ester, 29.2 per cent. Heat tends to increase the relative amount of *enol* present in this mixture. The rate of isomerization from *enol* → *keto* → *enol* is greater than in the case of ethyl acetoacetate but seems to vary in much the same way under the influence of different solvents, concentration, etc. The following table gives the relative amounts of *enol* present in methyl acetoacetate and related compounds and is of interest for purposes of comparison:

	Per Cent of *enol*
Methyl ester of acetoacetic acid	4.4
Methyl ester of methyl acetoacetic acid	3.16
Ethyl ester of brom acetoacetic acid	4.0
Diethyl ester of acetondicarboxylic acid	16.8
Acetylacetone [1]	80.4
Benzoylacetone	98–99

It may be added that molecular weight determinations of ethyl acetoacetate in chloroform by the freezing-point method show that it is still mono-molecular even at −62°.[2]

In summary it may be said that an exact knowledge of the character of *enol-keto* mixtures can be obtained only by the application of all available physical and chemical methods.[3] Among the chemical methods the so-called " brom-titration method " of K. H. Meyers has proved to be of great value. The method of ozonide decomposition, which has been developed by J. Scheiber and P. Herold [4] is also of importance since in cases where the structure of the compound under investigation is very complex it affords a point of attack in determining the constitution of the enolization products. Among the physico-chemical methods, refractometric methods,—thanks to the exact work of K. von Auwers and his students,—have been found to give excellent results and at the same time to be of general application.

[1] Ber., **44**, 2771 (1911).
[2] Annalen der Chemie, **352**, 147(1907).
[3] Annalen der Chemie, **415**, 169 (1917).
[4] Annalen der Chemie, **405**, 295 (1914).

CHAPTER XII

IONIZATION ISOMERISM

The subject matter presented under this title represents a special phase of tautomerism and desmotropism and forms part of the more general topic of molecular rearrangements to be considered later. It owes its development historically to the study of the constitution of aliphatic nitro-compounds:

According to Victor Meyer the structure of aliphatic nitro-compounds may be correctly represented by the formula $R \cdot CH_2NO_2$ since all of the chemical relationships of these substances are adequately represented in this way. Such a formula assumes, of course, that metallic derivatives have the constitution

$$\begin{matrix} R \cdot CHNO_2 \\ | \\ M \end{matrix} \qquad (M = \text{metal})$$

but this was in full accord with the chemical theory of the time, which supposed that hydrogen atoms in union with carbon could be directly replaced by alkali metals.

In 1888 A. Michael [1] came to the conclusion that if there were a choice between carbon and oxygen in the position to be occupied by a metallic atom in the process of salt formation, the choice would always fall to the oxygen. This conclusion was reached as the result of a study of the derivatives of ethyl acetoacetate, diethyl malonate, and other similar substances containing acidic methylene groups. Reasoning from analogy, Michael assigned the following formula to the sodium derivative of nitromethane:

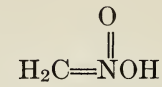
$$H_2C{=}N(=O)ONa$$

This conception soon found a zealous advocate in J. U. Nef,[2] who

[1] Jour. prakt. Chemie, **37**, 507 (1888).

[2] Annalen der Chemie, **270**, 330 (1892); **280**, 263 and 290 (1894); Ber., **29**, 1222 (1896).

believed that such substances were to be regarded as the salts of a hypothetical acid:

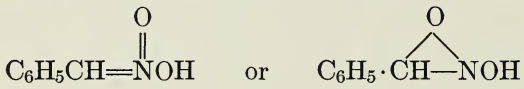


Experimental confirmation of this assumption was not obtained until 1895 when Holleman,[1] Hantzsch, and Schultze,[2] and also Konowalow[3] succeeded in isolating isomeric derivatives of certain aromatic nitromethanes, as, for example, $C_6H_5CH_2NO_2$. Isomerism of this kind was explained by supposing that desmotropic modifications such as

$$C_6H_5CH_2NO_2 \quad \text{and} \quad C_6H_5CH{=}NO\cdot OH$$

were formed. One of these substances was found to be a solid and was regarded as the labile form since it gradually rearranged to give a stable liquid modification. The solid reacted with phenylisocyanate, gave a color reaction with ferric chloride, and behaved in many ways as if an hydroxyl group were present, while the liquid form, on the other hand, showed none of these reactions. Both modifications behaved in a very remarkable way towards soda solutions. Solid, labile phenylnitromethane dissolved readily in cold aqueous sodium carbonate. The stable liquid variety, however, went into solution slowly and reluctantly, and its solution when acidified gave a precipitate of the isomeric labile form. This could be interpreted by assuming that rearrangement of the stable into the labile modification preceded the act of solution. At all events solution was evidently accompanied by a radical change in the constitution of the substance.

According to Hantzsch the labile modification of phenylnitromethane may be explained on the basis of either of the following two formulas:



since each represents an hydroxyl group as present in the molecule.

Of these the first is the one most generally accepted, but there is actually no way at present of distinguishing definitely between them. The stable modification, which is characterized by neutral reactions, is commonly assumed to possess the formula

$$C_6H_5CH_2NO_2$$

[1] Rec. trav. chim. des Pays-Bas, **14**, 129 (1895); **15**, 356 (1896); **16**, 162 (1897); Ber., **33**, 2913 (1900).

[2] Ber., **29**, 699, 2251 (1896); also compare Hantzsch, Ber., **33**, 2542 (1900).

[3] Ber., **29**, 2193 (1896).

These conclusions were naturally carried over into the field of the purely aliphatic nitro-compounds and the sodium derivative of nitromethane, for example, was represented by the formula:

$$H_2C{=}NOONa$$

This immediately raised the question as to the constitution of free nitromethane itself. If it is a true nitro-compound, i.e., CH_3NO_2, it must then be regarded as reacting tautomerically in the process of salt formation.

In an effort to solve this problem in the case of *m*-nitrophenyl-nitromethane A. F. Holleman [1] conceived the idea of applying conductivity measurements. He had observed that when an aqueous solution of *m*-nitrophenyl-nitromethane is treated with an equivalent quantity of hydrochloric acid, the solution is at first colored and then becomes colorless. This color change occupies only a few minutes and during this time the conductivity of the solution which is originally relatively high, decreases gradually but very noticeably. Even as early as 1895 Holleman suspected that *m*-nitrophenyl-nitromethane existed in two modifications and that of these the labile variety formed salts.[2]

Following this Hantzsch and his students determined the conductivity of a freshly prepared solution of phenylisonitromethane and found that while such a solution conducts electricity, its power to do so gradually decreases and finally completely disappears. This was interpreted as marking the gradual change of the isonitro into the true nitro-compound. Thus the sodium derivatives of nitromethane and nitroethane may be assumed to correspond respectively to the formulas

$$H_2C{=}NO\cdot ONa \quad \text{and} \quad CH_3CH{=}NO\cdot ONa$$

and their aqueous solutions when acidified should give primarily the free isonitro-compounds. In aqueous solution both

$$H_2C{=}NO\cdot OH \quad \text{and} \quad CH_3CH{=}NO\cdot OH$$

[1] Ber., **33**, 2913 (1900); also Ostwald, Jour. prakt. Chemie, **31**, 433 (1885); Zeitschr. physikal. Chemie, **3**, 170 and 418 (1889) and "Handbuch der physikal. Chemie"; Walker, Zeitschr. physikal. Chemie, **4**, 319 (1889); Bader, ibid., **6**, 289 (1890); Walden, ibid., **8**, 433 (1891); Bredig, ibid., **13**, 289 (1894); Holleman, Rec. trav. chim. des Pays-Bas, **14**, 129 (1895); **16**, 162 (1897); Henrich, Ber., **37**, 1406 (1904).

[2] Rec. trav. chim. des Pays-Bas, **14**, 129 (1895).

should conduct the electric current, but in the event of their transformation into the true nitro-compounds

$$CH_3NO_2 \quad \text{and} \quad CH_3CH_2NO_2$$

this property should vanish.

To test these conclusions Hantzsch devised the following quantitative experiment: starting with a dilute aqueous solution of sodium nitroethane, he added the exact equivalent of hydrochloric acid, whereupon a reaction took place according to the following equation:

$$CH_3CH{=}NO\cdot ONa + HCl \rightarrow NaCl + CH_3CH{=}NO\cdot OH$$

Since the process is instantaneous the result of mixing the two solutions is to give immediately a mixture of Na^+, Cl^-, H^+ and $(CH_3CH{=}NO\cdot O)^-$ ions and such a solution ought to be a better conductor than a solution of pure sodium chloride of the same concentration. It was found that, as a matter of fact, the conductivity of the reaction mixture was at first considerably greater than that of a solution of pure sodium chloride of the same concentration under similar conditions, but that this higher conductivity was not maintained and gradually decreased until finally it was exactly equal to that of a pure salt solution. This could happen only as a result of the combination of the positive and negative ions of the isonitro-compound to form undissociated nitroethane, viz.,

$$(CH_3CH{=}NO\cdot O)^- + H^+ \rightarrow CH_3CH_2NO_2$$

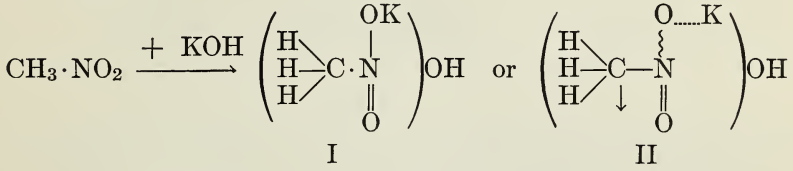
The reverse process may also be followed quantitatively by means of conductivity measurements. While strong acids react instantly with bases to form salts, true nitro-compounds usually react slowly since they must first be isomerized into the corresponding isonitro-derivatives. In order to follow the progress of this reaction Hantzsch mixed together equimolecular solutions of nitroethane and sodium hydroxide, measuring the conductivity of the reaction mixture from time to time. His results showed that in the beginning the conductivity of the solution was approximately that of pure sodium hydroxide, but that the hydroxyl ions decreased in quantity as more and more salt was formed.

$$CH_3CH_2NO_2 + Na^+ + OH^- \rightarrow (CH_3CHNO\cdot O)^- + Na^+ + H_2O$$

The reaction was accompanied by a gradual decrease in the conductivity of the mixture, which continued until the conductivity equaled that of a solution of the sodium derivative of nitroethane of the same concentration. Hantzsch was thus able to demonstrate that free nitroethane is a true nitro-compound and that while it seems to react with bases to

form salts it does not itself actually function in this reaction, but is first isomerized into the corresponding *enol* form. Substances of this kind, which are not actually acids, but which seem to react like acids, are called pseudoacids.

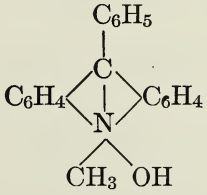
In order to account for the relatively great reactivity of the aci-nitro compounds, O. Baudisch [1] formulates the reaction by which such substances are formed from the corresponding nitro-compounds in the following way:



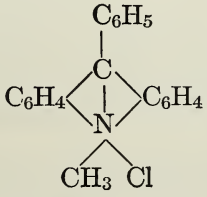
I II

The first formula corresponds to that which Werner has used to express the constitution of ammonium salts. The second indicates by means of a waving line that one of the valencies of nitrogen is different from the others, and by the arrow that the carbon atom approaches a trivalent condition. Even these additions fail to express fully the actual relationships between the atoms in the molecule, and at best it must be recognized that the constitutional formulas in current use give an inadequate representation of the substances for which they stand.

Certain organic compounds containing pentavalent nitrogen behave towards acids in a manner analogous to that which has just been described and are, therefore, called *pseudobases*. An example of such a substance is to be found in the cyclic quaternary base,

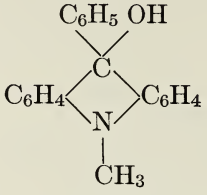


which is derived from methyl phenylacridinium chloride



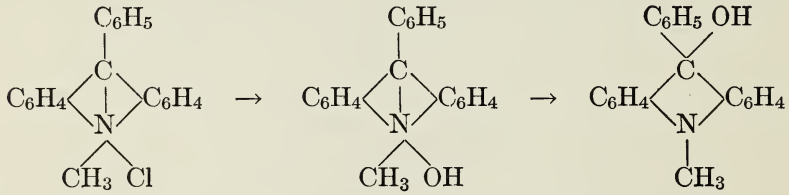
[1] Ber., **49**, 1162 (1916).

by replacing the chlorine atom by an hydroxyl group. Organo-ammonium bases are usually readily soluble in water and their solutions conduct the electric current. The above substance, however, exhibits none of these properties, being insoluble in water and completely neutral in all of its chemical reactions. In fact it behaves more like phenyl methyl acridol



than phenyl methyl acridinium hydroxide.[1]

In order to understand these discrepancies Hantzsch studied the reaction by means of conductivity measurements. His results show that the conductivity of the solution which is formed by mixing together equimolecular quantities of the chloride and potassium hydroxide is at first approximately equal to that of a solution of pure potassium hydroxide of the same concentration, but that this gradually decreases in value until it is finally equal to zero. Hantzsch explains this by supposing that the decomposition of methyl phenylacridinium chloride is accompanied by the formation of a true ammonium base and that this rearranges immediately to give an isomeric substance in which the hydroxyl group is in union with carbon.



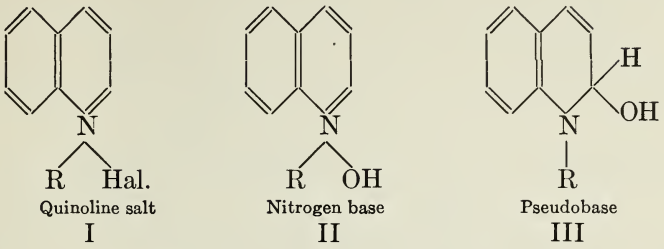
Such a substance shows no tendency to dissociate and is, in fact, a true pseudobase.[2]

Other illustrations of this type of substance are to be found among the derivatives of quinoline and isoquinoline. Thus when caustic alkali or moist silver hydroxide reacts with any of the salts of these substances the primary products of the reaction are true ammonium

[1] Compare rearrangement of NH_2 instead of OH in derivatives of ammonium amide, $H_4N \cdot NH_2$, Decker, Ber., **39**, 749 (1906); **46**, 969 (1913).

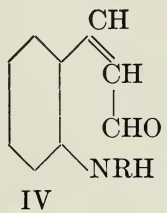
[2] Ber., **32**, 3109 (1899).

bases (II), but these rearrange immediately in aqueous solution to give pseudobases (III) [1]



Rearrangement products in which the hydroxyl groups are represented as in union with carbon are referred to by Decker as *oxydihydro* or *carbinol bases.*[2]

A. Kaufmann [3] has since shown that these carbinol bases behave like acyclic combinations and ascribes to them the tautomeric structure of amino aldehydes. According to his interpretation the pseudoammonium base III should be regarded as an *ortho* alkyl amino derivative of cinnamic aldehyde IV:



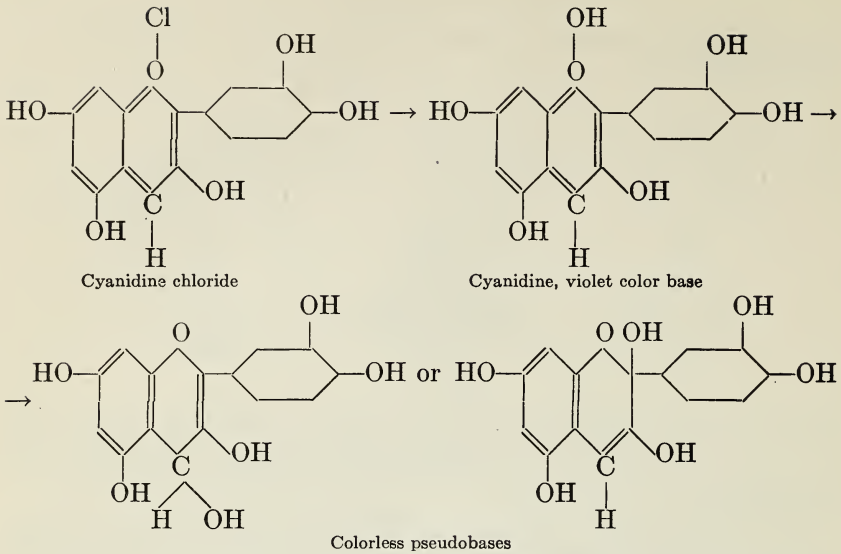
After Willstätter had recognized that the anthocyanines represent a large class of naturally occurring derivatives of the oxonium bases he discovered that the colored cyanidine chloride isomerizes into a colorless compound under the action of alkali. In other words, the colored base changes into a colorless pseudobase:[4]

[1] Hantzsch, Ber., **32**, 575 (1899).

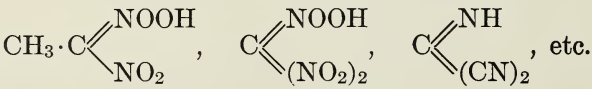
[2] Ber., **25**, 3327 (1892); see also Jour. prakt. Chemie, **47**, 28 (1893); Ber., **33**, 1715 (1900); Ber., **35**, 2588, 2589, 3068 (1902); Roser, Annalen der Chemie, **254**, 362 (1889); Freund, Ber., **22**, 2337 (1889).

[3] Kaufmann and Strübin, Ber., **44**, 680; Kaufmann and Play-Janini, Ber., **44**, 2670 (1911). See also Koenig, Jour. prakt. Chemie, **83**, 409 (1911).

[4] Compare Annalen der Chemie, **408**, 21 (1915).

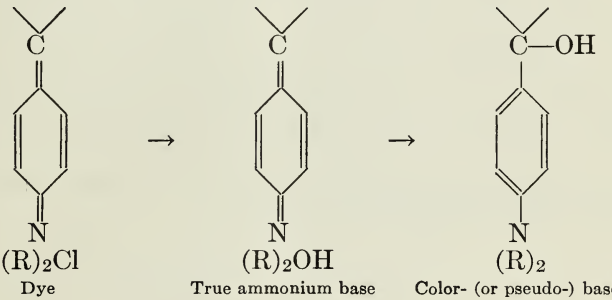


In such cases the molecule, which undergoes dissociation in solution, must be supposed to possess an entirely different constitution from the undissociated molecule. Pseudoacids and pseudobases represent organic combinations which are characterized by this type of isomerism, and Hantzsch uses the term "ionization-isomerism" [1] in order to differentiate this from other forms of tautomeric change. He has classified a great many substances among the pseudoacids which had previously been regarded as reacting directly with bases to form salts, and includes in this category all nitro-compounds in which at least one hydrogen atom is in union with the carbon atom to which the nitro group is attached, as, for example, $CH_3CH_2NO_2$, $(CH_3)_2CH \cdot NO_2$, $CH(NO_2)_3$, etc.; nitramines, $RNH \cdot NO_2$; nitrosamines, $R \cdot NH \cdot NO$; oximido-ketones, $>CO—\underset{|}{C}=NOH$; quinone oximes; hydroxyazo compounds; nitrophenols; etc. In all these and many other cases metallic derivatives are referred not to the usual formula of the substance but to an isomeric formula (*enol* modification), such as, for example:



[1] Compare Hantzsch and coworkers, Ber., **32**, 575, 3066 (1899); also Ber., **32**, 600, 607, 628, 641, 3137, 3148 (1899); **33**, 278, 752, 2542 (1900); **34**, 2506, 3142 (1901); **35**, 226, 249, 877, 883, 1001 (1902); **37**, 1076, 2705, 3434 (1904); **38**, 998, 1004, 2143, 2161 (1905); **39**, 139, 153, 1084, 1365, 2472, 2478, 3072, 3080, 4153; also 3149 (1906); also Zeitschr. physikal. Chemie, **48**, 289 (1904).

The color bases or carbinols derived from the rosaniline dyes may be regarded according to Hantzsch as pseudobases. Thus in the case of crystal violet, conductivity determinations on the system $R \cdot NCl + NaOH$ at zero degrees have demonstrated that at the beginning of the reaction the conductivity of the mixture was greater than that of sodium chloride of the same concentration. The observed conductivity at this time corresponded almost exactly to that of the system $RN^+ + Cl^- + Na^+ + OH^-$. This solution was colored and reacted strongly alkaline. It was observed that as the reaction proceeded these properties slowly disappeared and that the solution became colorless, the alkalinity became less, and the conductivity decreased until it finally became equal to that of sodium chloride. Hantzsch interpreted this by supposing that the primary product of the reaction is a true ammonium salt which gradually isomerizes to give a colorless, insoluble, undissociated carbinol combination or pseudobase.[1]

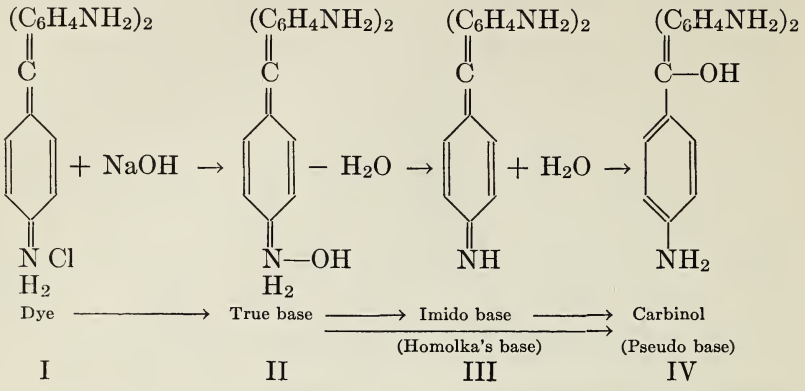


The maximum value for the conductivity, as compounded additively from the sum of the conductivities of the ions $Na^+ + Cl^- + XN^+ + OH^-$, was realized only in the case of one single substance—namely, crystal violet. Under similar conditions and even at zero degrees all other dyes examined gave low conductivity values and some approached or equaled that of pure sodium chloride. From these facts Hantzsch draws the conclusion that the isomerization of the true color base (of the ammonium type) into the pseudobase (of the carbinol type) takes place so rapidly that, even in the time required for the first conductivity measurement, the change is either almost or wholly complete.

A base which is characterized by solubility, strong basicity, etc., has recently been discovered by Homolka. This substance is formed as an intermediate when pararosaniline (new fuchsine) is decomposed by potassium hydroxide and, according to Hantzsch, may be regarded as

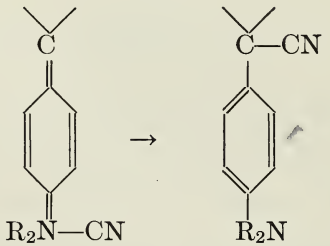
[1] Ber., **33**, 282 (1900).

an imidobase which is derived from the true ammonium base by loss of water:



Thus " when a dye (I) is treated with alkali the primary product is always a true ammonium base (II). This may either isomerize slowly to give the pseudobase (IV); or, due to the presence of an excess of alkali it may quickly lose water and form an imido base (III). The latter may then slowly add water to give the pseudobase."[1]

Hantzsch and Osswald discovered that other groups rearrange in the same way as hydroxyl and that in the case of cyclic quaternary cyanides the reaction may be expressed as follows:



According to Hantzsch intramolecular rearrangements of this type may be assumed in all cases where dyes of this class show conductivities which are lower than the ideal maximum values. He supposes that such reactions are instantaneous in cases where the initial conductivity of the reaction mixture equals that of sodium chloride.[2] Criteria other than those which have been mentioned must, of course, be considered, but none of those which have been suggested by Hantzsch is entirely satisfactory and some, at least, are generally discredited at the present time.

[1] Ber., **33**, 760 (1900); **37**, 3434 (1904).
[2] Ber., **32**, 578–579 (1899).

To recapitulate briefly: "when neutralization phenomena do not take place instantaneously but represent slow processes extending over a considerable period of time the presence of pseudoacids or pseudobases may be assumed." It does not follow, however, that the reverse process, whereby pseudoacids or bases are themselves formed from the salts of the true acid or base, is also a slow process. Indeed this change, as for example,

$$CH_3CH{=}NO\cdot ONa + HCl \rightarrow CH_3CH_2NO_2 + NaCl$$

may take place with such rapidity that it cannot be followed quantitatively.

It has been observed in the case of violuric acid and other oximidoketones that these combinations when heated exhibit abnormally large coefficients of conductivity and also abnormally large dissociation constants. It therefore seems probable that such substances possess at high temperatures different constitutions from those which are regularly assigned to their colored ions and salts. According to Hantzsch [1] "The presence of ionization-isomerism may be assumed in the case of all tautomeric substances which upon heating show increases in the value of their coefficients of conductivity and of their dissociation constants."

Hantzsch's theory in regard to pseudoacids and pseudobases has been outlined without reference to the objections which have been offered and continue to be offered to it by different investigators. It may be said in conclusion that such objections have not, for the most part, been directed against the main conceptions embodied in the theory which appear to be fundamentally sound and represent a valuable extension of the theory of tautomerism and molecular rearrangements. On the other hand, many of the methods which have been suggested as a means for recognizing phenomena of this sort have been rejected. The universality with which the theory has been developed by Hantzsch has also been subject to attack. References to this controversy may be found in a footnote [2] since it is impossible to consider the matter more fully at this time.

[1] Loc. cit.

[2] Zawidzki, Ber., **36**, 3334 (1903); **37**, 154; Hantzsch, Ber., **37**, 1076; Zawidzki, Ber., **37**, 2298 (1904); Bamberger, 2468; Hantzsch, 1084 and 2705 (1905); Kaufmann, Zeitschr. physikal. Chemie, **47**, 618 (1904); Ber., **37**, 2468 (1904); Ley and Hantzsch, Ber., **39**, 3149 (1906); Euler, Ber., **39**, 1607 (1906); Hantzsch, 2093; Euler, 2265; Hantzsch, 2703; H. Lundén, Zeitschr. physikal. Chemie, **54**, 532 (1906); Hantzsch, ibid., **56**, 57 (1906).

CHAPTER XIII

THE APPLICATION OF PHYSICO-CHEMICAL PRINCIPLES TO ORGANIC CHEMISTRY

During the first half of the last century the epoch-making discoveries of men like Gay-Lussac, Avogadro, Ampère, Faraday, Mitscherlich, Bunsen, Dulong, and Petit served to enrich both chemistry and physics. At that time most chemists were familiar with physical methods, but, as organic chemistry gradually differentiated itself from other branches of chemistry and began to develop into a separate science, it became more and more apparent that a knowledge of physical methods need not be the necessary equipment of a productive investigator in this field. In one of his lectures [1] W. Nernst describes how the physical apparatus which had originally been present in all chemical laboratories gradually became more and more superfluous until finally it vanished completely. For a long period of time organic chemists were absorbed with problems of structural organic chemistry. They learned that carbon is capable of forming a very great number of compounds with a relatively small number of elements and they gradually acquired such an exact insight into the constitution of organic molecules that they were able to describe the position and function of every atom. In this way structural and constitutional formulas were developed, and only then did it become obvious that a definite relation exists between certain physical properties of organic compounds and their structure or constitution.

In any study of the relationship which exists between the physical properties of a substance and its chemical constitution it is necessary in the first place to understand what is meant by the conception of additive properties. If two atoms of carbon combine with six atoms of hydrogen and one atom of oxygen to form C_2H_6O, for example, it is obvious that the molecular weight of the compound will equal the sum of the atomic weights and may be determined additively, viz.,

$$(2\times12) + (6\times1) + (1\times16) = 46$$

[1] Address at the dedication of the Institute for Physical- and Electro-Chemistry, Göttingen, 1896.

It does not in the least matter how these atoms are bound together in the molecule, the sum of their weights will always be the same. Thus weight, or mass, is a perfect additive property of the atoms present in any compound.

Other properties of the atoms have long been regarded as additive in character as, for example, molecular volume. This becomes clear by reference to the following table, where V represents the volume in cubic centimeters which 1 gram molecule of the substance occupies when measured at its boiling point:

Substance	V	Constant Difference
Formic acid	42	
Acetic acid	64	22
Propionic acid	86	22
Butyric acid	108	22

It is obvious that in this series of fatty acids the constant molecular difference of one carbon and two hydrogen atoms ($CH_2 = 14$) corresponds to a constant numerical increase in the value of V, the molecular volume. H. Kopp further made the discovery that in other series,—viz., hydrocarbons, alcohols, esters, aldehydes, and ketones,—the addition of CH_2 also increases the molecular volume of a substance by 22, so that in general it may be said that equal differences in composition (in this case CH_2) correspond to equal differences in the numerical value of the molecular volume.

Kopp also discovered that certain pairs of compounds, as, for example, $C_4H_{10}O$ and C_6H_6O, $C_5H_{12}O$, and C_7H_8O, etc., have the same molecular volume. In terms of the conceptions then held it was possible to imagine that in such compounds four atoms of hydrogen were exactly replaced by two atoms of carbon. Reasoning in this way Kopp concluded that, in general, one atom of carbon can replace two atoms of hydrogen without changing the molecular volume of the compound. Since, moreover, the molecular volume of CH_2 may be represented numerically by 22, and since two atoms of hydrogen equal one atom of carbon, it follows that the atomic volume of carbon will equal

$$\tfrac{2}{2}\tfrac{2}{2} = 11$$

while the atomic volume of hydrogen will equal

$$\tfrac{1}{2}\tfrac{1}{2} = 5.5$$

The atomic volumes of other elements have been obtained in a similar way and it has been found that O = 7.8, Cl = 22.8, Br = 29.1, I = 39.6, etc. It is thus possible to calculate the molecular volume of a given compound by finding the sum of the atomic volumes of the different atoms composing it. For example, the molecular volume of C_2H_6O should equal

$$(2\times 11)+(6\times 5.5)+(1\times 7.8)=62.8$$

and it has been found experimentally to equal 62.3.

In a great number of instances the calculated values agree very closely with the values which have been determined by experiment, but frequently they do not. The most conspicuous differences of this sort were first noted in connection with substances which contained oxygen. In the case of valeric acid, for example, the molecular volume as calculated equals 126.5 and as found, 130.5. Kopp explained this discrepancy as due to a difference in the nature of the union of the oxygen atoms and pointed out that oxygen has a different atomic volume when linked to carbon as carbonyl than when linked to hydrogen as hydroxyl. In the first case the atomic volume of oxygen equals 12.2, and in the latter, 7.8. By bearing this fact in mind and making the necessary correction for valeric acid, C_4H_9COOH, the value calculated for the molecular volume becomes

$$(5\times 11)+(10\times 5.5)+(12.2)+(7.8)=130.0$$

and corresponds closely with the experimental value, 130.5.

It was also found in the case of other elements that the values representing atomic volumes vary according to the form of combination in which the atom is found. Properties controlled in this way by constitution came to be known as " constitutive properties " in order to distinguish them from those properties which are purely additive in character.[1]

These and other investigations have made it possible to calculate with considerable accuracy the numerical values of many of the properties of a given organic substance, supposing that both the structure of the molecule and the additive and constitutive properties of the individual atoms are known. Indeed, in cases where a substance may be represented by two or more structural formulas, preference is usually given to that formula which shows the closest agreement between the

[1] Traube's work in this field is summed up in Ahrens' "Samml. Chem. u. Chem.-techn. Vorträge." Vol. IV (1899). See also Ber., **25**, 2524 (1892); **27**, 3173, 3179 (1894); **28**, 410, 2722, 2728, 2924, 3292 (1895); **29**, 2732 (1896); **30**, 265 (1897); **31**, 157 (1898); **40**, 130, 723, 734 (1907).

calculated and the experimental values of the physical constants of the substance. The molecular refraction and absorption of light have been of special service in solving many of the difficult problems of constitution. Indeed, so important has been the part played by spectrochemistry in the theory of organic chemistry that it is very desirable to consider this subject in some detail at this point.

The fact that a ray of light is always bent from a direct course when it passes from a less dense (air) into a more dense medium (glass, water, etc.) forms the basis of the science of spectroscopy. Different substances differ as to their power of refraction. Snell discovered in 1861 that a constant ratio exists between the sine of the angle of incidence (i) and the sine of the angle of refraction (r). This ratio is called the index of refraction (n) and is constant for the same pair of media, whatever the value of i happens to be. It is, moreover, equal to the ratio of the velocities of light (v and v_1) in the two media. Thus:

$$n = \frac{\sin i}{\sin r} = \frac{v}{v_1}$$

The refractive index of a substance varies considerably as a result of changes in physical state. In such changes density is by far the most important factor and several equations have been proposed in the effort to establish a definite relation between density and refraction. The first of these was based upon the emission theory of light, where

$$\frac{n^2-1}{d} = r = \text{a constant}$$

since according to Newton the expression n^2-1 represents a measure of the refractive power of a substance. With the development of the undulatory theory of light this first formula fell into disuse. It was attacked by Laplace who held that the ratio here represented depended upon conditions of temperature and was not, therefore, a constant. Arago and Biot believed, on the other hand, that it gave constant values for gases. Gladstone and Dale as well as Landolt [1] and Wüllner demonstrated that in the case of both liquids and solids the expression $\frac{n_2-1}{d}$ gave different values at different temperatures and was not therefore a constant. They maintained, however, that it could be used in a somewhat modified form,[2] namely:

$$\frac{n-1}{d} = r = \text{a constant}$$

[1] Poggendorf's Annalen der Chemie, **123**, 595 (1864).
[2] Poggendorf's Annalen der Chemie, **133**, 1 (1868).

and that it then gave constant values for liquids and solids at all temperatures. This was referred to as the Gladstone-Dale formula since it was empirically established by these investigators. It came to be quite universally accepted and is still in more or less general use among English chemists.

Since it is customary in chemistry to express constants in terms of gram molecules (m) instead of units of mass, specific refraction gave place to molecular refraction, viz.,

$$\frac{n-1}{d}m = \text{a constant}$$

This expression has, however, been superseded by a third which was advanced by H. A. Lorentz [1] and L. Lorenz [2] and which is in quite general use by European chemists at the present time

$$\frac{n^2-1}{(n^2+2)d} = \text{a constant}$$

H. A. Lorentz deduced this formula from Maxwell's electromagnetic theory of light. L. Lorenz, on the other hand, demonstrated that it could be derived from the undulatory theory of light on the assumption that the volume occupied by any given substance is not completely filled with matter, but that between the spherical molecules there are interstices through which light travels with the same velocity as through a vacuum. The molecular refraction of a substance equals in terms of the Lorentz-Lorenz formula

$$\frac{n^2-1}{n^2+2}\cdot\frac{m}{d} = M_\lambda$$

where λ signifies the particular wave length at which the value for n was determined. This is important since the index of refraction is different for different parts of the spectrum. The yellow sodium line is frequently used in such determinations or else the lines α, β, γ of the hydrogen spectrum. Under these circumstances M becomes M_D, M_α, M_β, M_γ, respectively.

If a ray of ordinary light undergoes refraction in a given medium it is broken up into homogeneous rays of different wave lengths. This phenomenon is known as dispersion. Thus when white light passes, for example, through a hollow prism which is filled with water it is broken up into the various colors of the spectrum. The distance

[1] Wiedem, Ann., **9**, 641 (1880).
[2] Ibid., **11**, 70 (1880).

from red to violet has been found to be always the same under like conditions for any given medium and in the case of water is equal to one centimeter. It is, however, different for different substances, and in the case of carbon bisulphide, for example, equals 6.5 cm. when measured under exactly the same conditions as give a value of 1 cm. for water. The former substance is thus said to possess a greater power of dispersion than water. This property is dependent upon the chemical nature of substances and is, in fact, more readily influenced by constitution than is the case with refractivity.

Dispersion is usually measured in terms of the difference between the indices of refraction of red and violet light of known wave lengths, as, for example, the hydrogen lines $\gamma(B)$ and $\alpha(H)$, that is by $n_\gamma - n_\alpha$. The dispersion of a substance depends upon its density, but Brühl [1] found that the formulas,

$$\frac{n_\gamma^2-1}{(n_\gamma^2+2)d}-\frac{n_\alpha^2-1}{(n_\alpha^2+2)d}=\text{specific dispersion}$$

and

$$\left(\frac{n_\gamma^2-1}{n_\gamma^2+2}-\frac{n_\alpha^2-1}{n_\alpha^2+2}\right)\frac{m}{d}=\text{molecular dispersion}$$

give values which are independent of temperature, density, and state of aggregation.

According to Brühl changes in structure or, in other words, changes in the combinations of the atoms, are usually much more strikingly apparent from values representing the dispersions than from corresponding values representing the refractions of organic compounds. For this reason in modern chemical literature the dispersion of a substance is usually given along with its specific and molecular refractions. It may be added that Auwers and Eisenlohr [2] have recently recommended that multiples of 100 times the specific refraction be used instead of molecular refractions. These values are represented by the symbols Σ_α, Σ_D, etc., and are supposed to be a better guide in interpreting the phenomena of optical exaltations than are the corresponding refractions.

In determining the index n_λ, from which both specific and molecular refractions and dispersions are calculated, it is very important that the temperature should be kept constant, and usually at 20°. The Pulfrich

[1] Zeitschr. physikal. Chemie, **7**, 140 (1891).

[2] Ber., **43**, 809 (1910); also see W. A. Roth and F. Eisenlohr, "Refraktometrisches Hilfsbuch," Leipzig, 1911, Veit & Company.

refractometer is especially convenient for colorless or only slightly colored substances, since it affords an easy means of regulating temperatures, while sodium and hydrogen (red and violet) may be used as the sources of light. At a given temperature the observed angle should remain constant. Should it change and, for example, become increasingly greater, this would indicate that polymerization was taking place and the experiment would cease to have any value.

The specific gravity—or what is the same in this case, the density—must also be determined very accurately, and for this purpose Ostwald's pyknometer, which holds about 3 cc., is found most serviceable. The temperature at which density is determined must obviously be the same as that for the index of refraction. The density compared with water at 4° C. must also be given and atomic refractions must be calculated on this basis. In calculating densities it is unnecessary to correct for a vacuum, although this is, of course, the more accurate procedure. Also Auwers and Eisenlohr recommended molecular weights calculated to four figures, rather than those represented by round numbers. Because of the possibility of polymerization it should always be stated whether the operation immediately followed the purification of the substance, and if not how much later.

The refraction of organic compounds has been the subject of very careful study for the past fifty years, and as a result the relation which exists between this physical property of a substance and its chemical structure is better known than in the case of any other physical properties. The first efforts of investigators in this field were focused upon the additive aspects of the problem. The question as to whether the refraction of light is a property of the mass of the atoms in the molecule or whether it depends upon the form of combination as well, was investigated as early as 1864 by Landolt who found that isomeric eompounds possess almost identical refractions. In comparing the molecular refraction of glycerine, $C_3H_8O_3$ (34·32), with that of mixtures corresponding to the same empirical formula—as, for example, $CH_3COOH + CH_3OH$ and $HCOOH + C_2H_5OH$—he discovered almost identical values in all cases and, therefore, concluded that refraction was a purely additive function of the atoms. Reasoning on this basis it was possible to calculate the values represented by the atomic refractions of the different elements. Thus since the molecular refraction of methyl alcohol, CH_4O, is 13.17 and that of acetaldehyde, C_2H_4O, is 18.58, and since these two substances differ by but a single carbon atom, it follows that the difference in their molecular refractions, or 5.41, must represent the atomic refraction of an atom of carbon. In the same way the difference in the molecular refractions of acetaldehyde, C_2H_4O, and

ethyl alcohol, C_2H_6O, which differ by two hydrogen atoms, gives the atomic refraction for hydrogen, viz.,

$$20.7 - 18.58 = 2.12 \div 2 = 1.06$$

The mean of a great many experiments has furnished the following values for atomic refractions: C = 5, H = 1.3, O = 3.

The molecular refractions of such substances as alcohols, ethers, and acids, as calculated from the sum of their atomic refractions, agree very closely with the values which have been obtained as the result of experiment. In the case of other organic compounds, however, the differences between the calculated and the experimental values for molecular refractions are so great that Landolt was forced to the conclusion that the property of refraction is not, as a matter of fact, purely additive in character. He found, however, that in the case of any given homologous series the molecular refractions, like the molecular volumes of the substances, increase regularly with the increase in the number of carbon atoms. Thus in the case of alcohols, ethers, and acids the increase in molecular refraction in any series is almost a constant. It equals 7.2 and corresponds to an increase of CH_2.

Landolt, and quite independently Gladstone and Dale,[1] were then able to demonstrate that changes in the atomic grouping in the case of isomeric substances exercise a small but perfectly definite and measurable effect upon molecular refraction, an effect which cannot possibly be accounted for on the basis of experimental error. "Every liquid has a specific refraction composed of the specific refractions of its component elements, modified by the manner of combination but unaffected by changes of temperature." This marks the definite discovery of constitutive differences in refraction.

Since 1880 knowledge along these lines has been actively developed and constitutive influences have come to be better understood. This is in large measure due to the investigations of Brühl,[2] who has added greatly to the material collected by earlier investigators, and has applied this material in the elucidation of many problems of structural chemistry. Brühl has been able in the first place to demonstrate that fluctuations in molecular refraction do not depend upon the neutral, acid, or basic properties of the substances in question, and in the second place to assign a definite value to the constitutive influence of double bonds between carbon atoms. The latter was found to be fairly constant, although it varied in different compounds between 1.63 and 2.17. Thus, for

[1] Phil. Trans., **148**, 8 (1858); **153**, 323 (1863).

[2] Zeitschr. physikal. Chemie, **7**, 140 (1891); Jour. prakt. Chemie, **50**, 152 (1894).

example, the molecular refractions of unsaturated organic compounds show higher values than those calculated from the sum of the refractions of the component atoms, and the more unsaturated the compound the greater the deviation from normal. In the case of benzene the molecular refraction as calculated is:

Atomic refraction of C =	$5\times6=30.0$
Atomic refraction of H =	$1.3\times6=7.8$
Molecular refraction (calculated)	37.8
Molecular refraction (found)...	43.7
Deviation.....	5.9

If it may be assumed on the basis of the Kekulé formula that benzene contains three unsaturated double bonds in its molecule, the refractive value of a single ethylene linkage may be found by dividing 5.9 by 3 and, roughly, equals 2. This value is referred to as the "increment" for the double bond between carbon atoms, and must be added to the sum of the atomic refractions in calculating the molecular refractions of unsaturated compounds. It is commonly represented by the symbol ⊏. The increment for a triple bond has also been determined. It is represented by the symbol ⊨ and is somewhat greater in value than ⊏, being equal to 2.2.

To account for minor fluctuations in atomic refractions Brühl goes so far as to suggest that there are small structural differences peculiar to each compound which affect individually each atom in the molecular. The refraction for oxygen is markedly different for different states of combination. Thus oxygen, when present in substances in the form of carbonyl, hydroxyl, or ether, respectively, shows different and characteristic values, so that in computing the molecular refraction of a given compound containing oxygen it is necessary to use different figures to represent each of these three states of combination. The atomic refraction of nitrogen varies even more than that of oxygen, and this variation is often very difficult to explain.

The value of the science of spectrochemistry in determining questions of constitution in structural organic chemistry was fully demonstrated by the investigations of Brühl. After his death this side of the work was further developed by K. Auwers and F. Eisenlohr,[1] who, in re-examining the very foundations of the science, were able to add to

[1] Ber., **43**, 806 (1910); Jour. prakt. Chemie, **82**, 65 (1910); **84**, 1, 37 (1911); Annalen der Chemie, **387**, 165, 200, 240; **408**, 212 (1915); **409**, 149 (1915); **410**, 287 (1915); **413**, 253 (1917); Ber., **46**, 494 (1913); **48**, 1357, 1377 (1915); **49**, 827 (1916).

the experimental material upon which many of its deductions rest. Through their efforts research in this field has kept pace with the more recent developments in structural theory. Up to this time Conrady's figures for the D-line and Brühl's values for the lines Hα, Hβ, Hγ had been in general use, although they had not been found satisfactory in all respects, but they were now completely replaced by the values for atomic refraction, dispersion, and increments which had been recalculated by Auwers and Eisenlohr [1] and which may be found in the following table:

		Atom. Wgt.	H_α	D	H_β	H_γ	$H_\beta - H_\alpha$	$H_\gamma - H_\alpha$
Group CH_2	CH_2	14.02	4.598	4.618	4.668	4.710	0.071	0.113
Carbon	C	12.00	2.413	2.418	2.438	2.466	0.025	0.056
Hydrogen	H	1.01	1.092	1.100	1.115	1.122	0.023	0.029
Carbonyl-oxygen	O''	16.00	2.189	2.211	2.247	2.267	0.057	0.078
Ether-oxygen	O<	16.00	1.639	1.643	1.649	1.662	0.012	0.019
Hydroxyl-oxygen	O'	16.00	1.522	1.525	1.531	1.541	0.006	0.015
Chlorine	Cl	35.46	5.933	5.967	6.043	6.101	0.107	0.168
Bromine	Br	79.92	8.803	8.865	8.999	9.152	0.211	0.340
Iodine	I	126.92	13.757	13.900	14.224	14.521	0.482	0.775
Ethylene bond	╒	..	1.686	1.733	1.824	1.893	0.138	0.200
Acetylene bond	╞	..	2.328	2.398	2.506	2.538	0.139	0.171
Nitrogen in prim. aliphatic amines	=N—C	14.01	2.309	2.322	2.368	2.397	0.059	0.086
N. in secondary aliphatic amines	$-N<^{C}_{C}$	14.01	2.475	2.499	2.561	2.603	0.086	0.119
N. in tertiary aliphatic amines	$N<^{C}_{C}<^{C}_{C}$	14.01	2.807	2.840	2.940	3.000	0.133	0.186
Nitrogen in nitriles	N≡C	14.01	3.054	3.070	3.108	3.129	0.055	0.065

The elucidation of the many problems of structural organic chemistry has been attempted by the application of spectrochemical considerations. The question of the constitution of ethyl acetoacetate may be mentioned in particular as illustrating the way in which this method may be used in determining the structure of organic compounds. As is known, two different formulas are possible for this substance, namely,

$$CH_3COCH_2COOC_2H_5 \quad \text{and} \quad CH_3C(OH) : CHCOOC_2H_5$$

[1] Zeitschr. physikal. Chemie, **75**, 585 (1911); also "Refraktometrisches Hilfsbuch," p. 128.

The difference between these two formulas may be expressed in terms of atomic refractions and increments as follows:

$$C_6H_{10}O_2^{\cdot\cdot}O< \quad \text{and} \quad C_6H_{10}O^{\cdot\cdot}O^{\cdot}O<\overline{\underset{1}{\vdash}}$$

If the molecular refraction of each of these is calculated for light of wave length D the following results are obtained:

Keto Form	Enol Form
$C_6 = 6\times2.418=14.508$	$C_6 = 6\times2.418=14.508$
$H_{10} = 10\times1.100=11.000$	$H_{10} = 10\times1.100=11.000$
$O^2 = 2\times2.211= 4.422$	$O^{\cdot\cdot} = 1\times2.211= 2.211$
$O< = 1\times1.643= 1.643$	$O^{\cdot} = 1\times1.525= 1.525$
	$O< = 1\times1.643= 1.643$
	$\overline{\underset{1}{\vdash}} = 1\times1.733= 1.733$
Mol. refraction $=31.573$	Mol. refraction $=32.620$

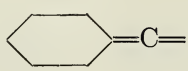
The molecular refraction for ordinary ethyl acetoacetate as determined at room temperature has been found to be $M=32.00$.[1] This value is obviously intermediate between the calculated values for the *keto* and *enol*, respectively, although it approximates the former more closely than the latter. These results thus tend to confirm chemical investigation in the matter since they indicate that liquid ethyl acetoacetate consists of a mixture which contains a large amount of the *keto* modification together with small quantities of ethyl β-hydroxycrotonate.

In the case of certain groups of unsaturated compounds abnormal molecular refractions and dispersions have been observed, which greatly exceed the calculated values even after all possible increments have been added. Such unusual deviations are referred to as optical anomalies or exaltations, and are frequently observed in the case of substances with one or more ethylene linkages in immediate proximity to the benzene ring. Thus, for example, $C_6H_5CH_2CH{=}CH_2$ shows normal, while $C_6H_5CH{=}CHCH_3$ shows abnormal molecular refraction. Even more striking illustrations of phenomena of this kind have been discovered by Brühl[2] in the case of cinnamyl derivatives as, for example:

[1] Ber., **44**, 3530 (1911).
[2] Ber., **40**, 883 (1907).

	Calculated	Found	Dispersion
$C_6H_5CH{=}CH\cdot CHO$ Cinnamic aldehyde	$C_9H_8O^{\cdot\cdot}\overline{\vert}_4$ $M_\alpha = 39.78$	$M_\alpha = 43.51$	$M_\gamma - M_\alpha$ Found $= 4.17$ Calc. $= 1.65$
$C_6H_5\cdot CH{=}CH\cdot C\begin{cases}O\\OC_2H_5\end{cases}$ Cinnamic ester	$C_{11}H_{12}O^{\cdot\cdot}O<\overline{\vert}_4$ $M_\alpha = 50.58$	$M_\alpha = 53.62$	$M_\gamma - M_\alpha$ Found $= 3.82$ Calc. $= 1.88$
$C_6H_5\cdot CH{=}CHCH$ $\Vert$ $CH\cdot C\begin{cases}O\\OH\end{cases}$ Cinnamylidene acetic acid dissolved in acetone	$C_{11}H_{10}O^{\cdot}O^{\cdot\cdot}\overline{\vert}_5$ $M_\alpha = 50.06$	$M_\alpha = 60.42$	$M_\gamma - M_\alpha$ Found $= 9.70$ Calc. $= 2.04$

Other instances of this sort were discovered by Eijkmann among the derivatives of propenyl, by Tschugaeff among trimethylene derivatives, and by Wallach among substances possessing so-called semi-cyclic double bonds as illustrated, for example, in combinations containing the atomic grouping:



These last two discoveries have both been confirmed by the work of Auwers and Eisenlohr.

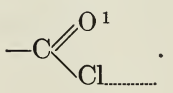
In reviewing the situation Brühl pointed out that optical anomalies are most frequently met with in the case of substances containing two unsaturated ethylene linkages (or one ethylene and one carbonyl) in adjacent positions. In attempting to explain the phenomena Brühl applied the conceptions of Thiele's theory of partial valency, which was attracting a great deal of attention at the time, and pointed out various relationships which tended in his opinion to establish connection between optical anomaly and the presence of conjugated systems of double bonds in the molecule.[1] Auwers and Eisenlohr have since shown, however, that at least some of Brühl's conclusions must be discounted, because many of the relationships to which he refers have proved far more complicated in character than he could possibly have sensed from the data known at that time. The general status of the

[1] Ber., **40**, 900 and 1160 (1907).

problem may be summed up by saying that Brühl was able to show conclusively that the molecular refraction of a substance depends upon the relative position of the double bonds functioning in the molecule; and in those cases where more than one unsaturated linkage is present he demonstrated that an arrangement represented by systems of so-called conjugate double bonds corresponds to abnormally high molecular refractions and dispersions. Illustrations of this, which might be greatly augmented in number, are to be found in the following table. It should be noted that figures expressing anomalies are printed in heavy type:

	M_α	$M_\gamma - M_\alpha$
$CH_2{=}CH\cdot CH_2\cdot CH_2\cdot CH{=}CH_2$ Diallyl $C_6H_{10}\overline{\vert}_2$	Found = 28.77 Calc. = 28.89 **−0.12**	Found = 1.00 Calc. = 1.05 **−0.05**
$CH_3.CH{=}CH\cdot CH{=}CH\cdot CH_3$ Isodiallyl $C_6H_{10}\overline{\vert}_2$	Found = 30.38 Calc. = 28.89 **+1.49**	Found = 1.57 Calc. = 1.05 **+0.52**
CH_3O—C$_6$H$_4$—$CH{=}CH{-}CH_3$ Anethole $C_{10}H_{12}O < \overline{\vert}_4$	Found = 47.70 Calc. = 45.89 **+1.81**	Found = 2.95 Calc. = 1.75 **+1.20**
CH_3O—C$_6$H$_4$—$CH_2{-}CH{=}CH_2$ Methylchavicole $C_{10}H_{12}O < \overline{\vert}_4$	Found = 45.95 Calc. = 45.89 **+0.06**	Found = 2.04 Calc. = 1.75 **+0.29**

Perfectly definite, albeit relatively small, optical anomalies have also been observed in the case of substances which contain an unsaturated atom in direct union with a carbonyl or ethylene group, as in the radical



[1] Ber., 44, 3514, 3525 (1911); also 3188 and 3679.

While the refractions of substances containing unsaturated atoms in conjugate positions usually exhibit exaltations, there are, nevertheless, important exceptions to this general rule. It has been observed, for example, that substitution in certain positions seems to diminish the optical exaltation of a substance; and this fact becomes even more strikingly apparent if figures are compared which express 100 times the specific refractions and dispersions, viz., Σ_D and $\Sigma_\gamma - \Sigma_\alpha$. An illustration of this is to be found in the case of the two isomeric diisopropenyls which differ only as regards the relative positions occupied by the methyl groups and whose optical exaltations are given in the following table:

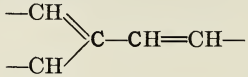
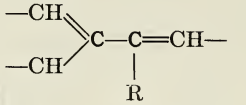
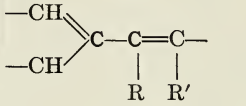
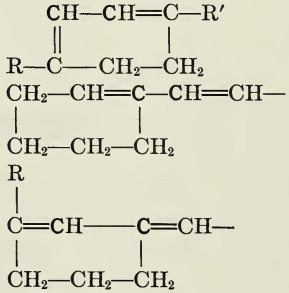
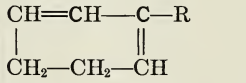
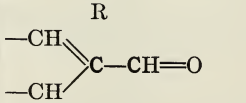
	Exaltation		Exaltation	
	M_D	Σ_D	$M_\gamma - M_\alpha$	$\Sigma_\gamma - \Sigma_\alpha$
$CH_3 \cdot CH{=}CH{-}CH{=}CH{-}CH_3$	+1.71	+2.08	+0.52	+0.63 = 50%
$H_2C{=}C{-}C{=}CH_2$ (with CH_3 on each C); Diisopropenyl $C_6H_{10}\|^{=}_{2}$	+0.82	+1.00	+0.37	+0.45 = 35%

A comparison of the figures shows an appreciable decrease in exaltation in the case of the second isomer.

Indeed Auwers and Eisenlohr[1] are of the opinion that, in general, disturbances in conjugate systems due to substitutions tend to diminish the optical exaltation of the substance. This effect upon a conjugate system is not restricted to alkyl groups, but extends to hydroxy, methoxy, and ethoxy groups as well. These authors conclude that a sharp line cannot be drawn between normal and abnormal compounds, but that there is a transition from one to the other. Thus the disturbances produced by substitutions may be such as to completely neutralize the optical exaltation, and under such circumstances a substance which possesses a conjugate system of double bonds might show perfectly normal optical properties. These points must all be very carefully borne in mind in the application of spectroscopy to the determination of structure if serious errors are to be avoided. The following table shows the influence of substitution upon several types of conjugate

[1] Ber., **43**, 806 (1910); Jour. prakt. Chemie, **82**, 65 (1910); Jahrb. der Radioaktivität, **9**, 333 (1912).

systems. The symbols $E\Sigma$-Refr. and $E\Sigma$-Disp. represent values 100 times as great as the specific refractions and dispersions respectively:

Class of Compound	Conjugate System	$E\Sigma$-Refr.	$E\Sigma$-Disp.
Aliphatic hydrocarbons	—CH=CH—CH=CH—	1.90	50%
	—CH=CH—C(R)=CH—	1.10	....
Styroles		1.10	45%
		0.70	30%
		0.45	20%
Hydroaromatic hydrocarbons		0.8–1.2	40%
		0.25	20%
Aldehydes, Acyclic	—CH=CH—CH=O	1.80	50%
	—C(R)=CH—CH=O	1.25	45%
	—CH=C(R)—CH=O		
Aldehydes, Cyclic		1.00	45%

Class of Compound		Conjugate System	$E\Sigma$-Refr.	$E\Sigma$-Disp.
Ketones	Acylic	—CH=CH—C(R)=O	0.90	30–40%
	Acyclic and Cyclic	—C(R′)=CH—C(R)=O	0.85	
		—CH=C(R′)—C(R)=O	0.50	....
Acids		—CH=CH—C(OH)=O	1.10	40%
		—CH=C(R)—C(OH)=O	0.80	....
Esters		CH=CH—C(OR)=O	0.80	30%
		—CH=C(R′)—C(OR)=O	0.50	20%

In cases where ethylene, or other unsaturated linkages possess an atom in common, as, for example, in the system C=C=C, the substance shows normal or nearly normal refraction. The same is true when the double bonds are widely separated in the molecule.

Where two or more conjugate systems of double bonds are present in the same molecule two distinct arrangements are possible, viz.,

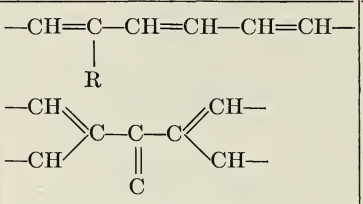
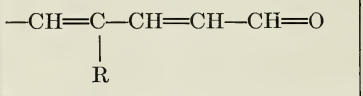
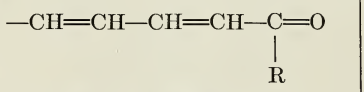
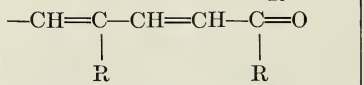
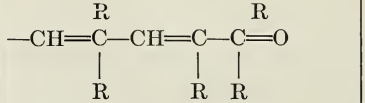
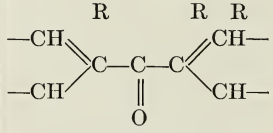
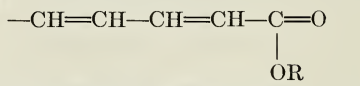
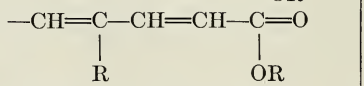
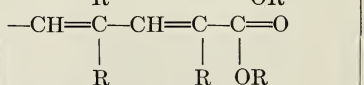
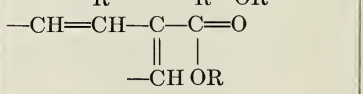
—C=C—C=C—C=C—, O=C—C=C—C=O etc.,

and

—C=C—C(C=C)=C— —C=C—C(C=O)=C—, etc.

These and analogous systems are called, respectively, "cumulative conjugate systems" and "crossed conjugate systems." The effect of such systems on refraction is radically different, the former producing an extraordinary increase in optical exaltation, while the latter causes optical depression. These relationships are much more complicated than in the case of simple conjugate systems and no exact rules

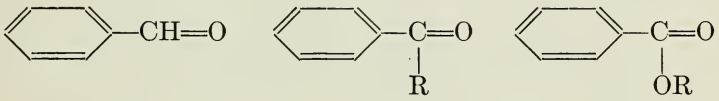
have as yet been formulated in regard to them. At best exaltations can only be appraised roughly and cannot as yet be represented by exact increments. The following table gives the mean values for certain types of atomic groupings as determined by Auwers and Eisenlohr,[1] and such values may serve in certain instances as a basis for calculations:

Class of Compound	Conjugate System	$E\Sigma$-Refr.	$E\Sigma$-Disp.
Hydrocarbons		3.4	130%
		1.0	40%
Aldehydes		3.3	150%
Ketones		3.3	145%
		2.7	110%
		2.1	95%
		1.0	45%
Esters		2.4	120%
		2.0	100%
		1.5	75%
		0.5	25%

[1] Jour. prakt. Chemie, **84**, 37 (1911).

The statement that the presence of cumulative conjugate systems leads to an increase in the optical exaltation of a substance is not without important exceptions. Benzene, which in a sense may be said to have such an arrangement of atoms in the molecule, shows no exaltation and may therefore be said to possess a *neutral* conjugate system. Derivatives of benzene vary greatly as to their refraction, showing in some cases a very slight and in other cases a very great exaltation. For example, certain phenols and their ethers exhibit such slight divergence in optical properties that they cannot be said to possess constitutive differences. This is also true in the case of certain isomeric alkyl derivatives of benzene. If, on the other hand, the substituent in the benzene ring consists of an unsaturated group, active conjugate systems may arise.

K. Auwers has recently investigated the subject of position isomerism in its relation to spectro-chemistry and has obtained results which are very valuable in their bearing upon problems of constitution. Aromatic aldehydes, ketones, and esters,



were selected for observation and the effect of substitution in the *ortho*, *meta*, and *para* positions was studied in the case of a large number of different substituents. As the above formulas indicate these substances all show active conjugate systems. It was found that the introduction of methyl in the *ortho* and *meta* positions produced only insignificant changes in the optical constants of the substance, but that substitutions in the *para* position were accompanied by marked exaltations. This is a very general rule and holds in the case of all substitutions of methyl which have been observed up to the present time.

Substitutions of the methoxy group also produce the greatest effect when they take place in the *para* position; but in this case the influence of the substituent in the *ortho* and *meta* positions is more marked than in the case of methyl. The values given in the following table which show the dispersions of the various substances are especially interesting in this connection. It will be noted that the highest values are always those of *para* substitution products and that they therefore afford a definite method for identifying these substances. The *ortho* and *meta* substitution products cannot be distinguished in this way.

TABLE I—METHYL DERIVATIVES

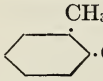
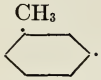
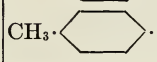
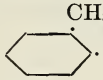
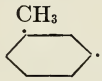
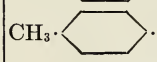
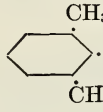
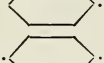
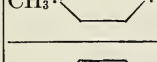
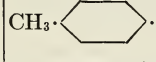
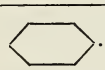
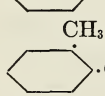
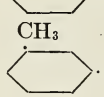
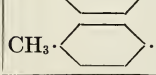
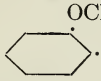
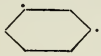
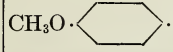
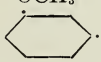
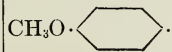
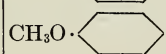
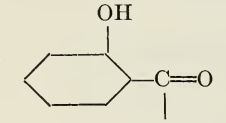
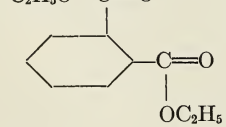
No.	Formula	d_4^{20}	n_D^{20}	$E\Sigma_\alpha$	$E\Sigma_D$	$E\Sigma_\beta - \Sigma_\alpha$ %	$E\Sigma_\gamma - \Sigma_\alpha$ %
1		1.046	1.5452	+0.99	+1.01	+45	+49
2		1.038	1.5483	+0.93	+1.01	+48	+53
3		1.022	1.5416	+1.10	+1.18	+49	+54
4		1.018	1.5460	+1.37	+1.47	+58	+64
5		1.027	1.5338	+0.60	+0.65	+32	+35
6		1.014	1.5320	+0.51	+0.57	+33	+36
7		1.007	1.5306	+0.66	+0.73	+37	+41
8		1.004	1.5342	+0.95	+1.01	+42	+47
9		0.995	1.5294	+0.72	+0.77	+36	+39
10		1.010	1.5272	+0.43	+0.48	+29	+31
11		0.991	1.5275	+0.77	+0.82	+38	+42
12		0.984	1.5177	+0.51	+0.53	+28	+31
13		0.969	1.5192	+0.80	+0.86	+40	+44
14		1.047	1.5056	+0.43	+0.49	+26	+26
15		1.033	1.5077	+0.49	+0.53	+27	+30
16		1.028	1.5057	+0.58	+0.62	+28	+31
17		1.026	1.5081	+0.73	+0.77	+33	+35

TABLE II—METHOXY DERIVATIVES

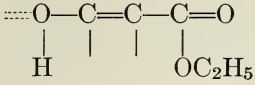
No.	Formula	d_4^{20}	n_{20}^{D}	$E\Sigma_\alpha$	$E\Sigma_D$	$E\Sigma_\beta - \Sigma_\alpha$ %	$E\Sigma_\gamma - \Sigma_\alpha$ %
1		1.046	1.5452	+0.99	+1.01	+45	+49
2		1.133	1.5598	+1.10	+1.21	+79	+91
3		1.118	1.5538	+1.17	+1.27	+67	..
4		1.123	1.5731	+1.81	+1.97	+95	..
5		1.027	1.5338	+0.60	+0.65	+32	+35
6		1.088	1.5395	+0.89	+0.97	+53	+59
7		1.095	1.5410	+0.73	+0.82	+51	+55
8		1.099 (?)	1.5564	+1.33	+1.45	+75	+81
9		1.087	1.5163	+0.43	+0.45	+24	+24
9a		1.047	1.5056	+0.43	+0.49	+26	+26
10		1.156	1.5340	+0.67	+0.72	+39	+43
10a		1.111	1.5213	+0.69	+0.73	+37	+42
11		1.100	1.5152	+0.68	+0.73	+38	+43
12		1.103	1.5544	+0.97	+1.04	+52	+57

If the two preceding tables are compared it appears that the differences between the *ortho* and the *meta* substitution products, on the one hand, and the *para* substitution products, on the other hand, are best shown by the specific refractions in the case of methyl and by the respective dispersions in the case of the methoxy derivatives. This is due to the fact that the relation between the densities and the specific refractions is different in the case of these two groups of substances. If, for example, the density decreases while the index of refraction remains approximately the same, the change will be accompanied by an increase in the molecular refraction, but by no appreciable change in the value representing the dispersion. If, on the other hand, as happens in the case of the methoxy substitution products, the density decreases very slightly while the index of refraction increases rapidly, the change will be accompanied by an increase, both in the molecular refraction and dispersion.

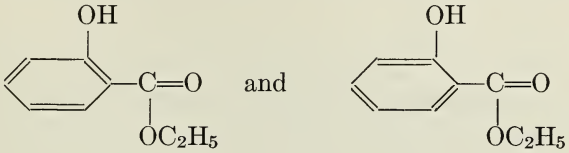
Brühl had observed that the substitution of hydroxyl in the benzene ring is often accompanied by optical exaltation and, on the assumption that the hydroxyl group is unsaturated, had explained the phenomenon as due to the formation of an *active* conjugate system. Later the question was reopened by Auwers who discovered that phenol and its homologues differ only very slightly in optical properties from the corresponding hydrocarbons from which they are derived. It is true that polyhydric phenols show exaltations, but from the point of view of constitution the most important exaltations are those which result from the introduction of hydroxyl into derivatives of benzene which already possess unsaturated groups in the side chain. Under these conditions the " unsaturated " hydroxyl group is optically more effective than the other unsaturated substituents as a comparison of the following two compounds shows:

Formula	$E\Sigma_\alpha$	$E\Sigma_D$	$E\Sigma_\beta - \Sigma_\alpha$	$E\Sigma_\gamma - \Sigma_\alpha$
	+0.84	+0.90	+56%	+64%
	+0.56	+0.58	+23%	+25%

In the case of the salicylic ester the marked exaltation may be explained on the assumption that the following system is present in the molecule:



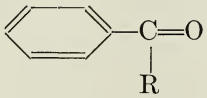
This supposes that salicylic ester has the first of the two possible formulas,



or else that more of the first than of the second kind of molecules are present in an equilibrium mixture of the two.

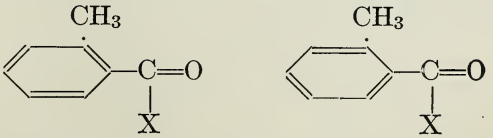
It is obvious from what has been said that spectro-chemistry affords a more delicate and exact method for determining important questions of constitution than any other single method which is known at the present time.

In continuing the study of benzene derivatives which possess active conjugate systems as, for example,



Auwers came to the conclusion that in spite of the fact that one of the three ethylene linkages of benzene is *active* in such compounds, the other two continue to be optically neutral in character.[1] While such a condition seems at first sight improbable and is difficult to account for in terms of theory, it is, nevertheless, in general agreement with the observed relationships. The following considerations serve to illustrate this point:

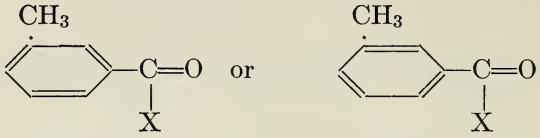
The substitution of a saturated radical (alkyl) in the *ortho* position to the unsaturated substituent should under such conditions cause no optical disturbances since the constitution of the derivative in question must correspond to either one or the other of the following formulas



I. II.

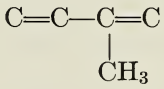
[1] Annalen der Chemie, **408**, 230 and following (1915).

and the methyl is not, therefore, in a position to exert any appreciable influence upon either the *active* conjugate system C=C—C=O, or upon the *neutral* system C=C—C=C. If substitution takes place in the *meta* position, the resulting product may be represented by either

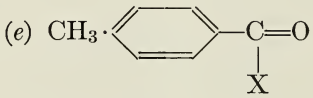


III. IV.

In this case the optical effect of substitution cannot be predicted since a substance constituted like III. would not differ optically from the substance from which it was derived, while one corresponding to IV. would be expected to show increased optical exaltation. This would follow from the fact that the substitution of methyl in the following position

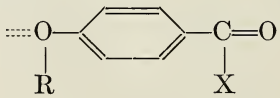


would tend to disturb the equilibrium of the *neutral* system. Substitution in the *para* position



might be expected from every point of view to produce disturbances which would be accompanied by increased optical exaltation. This deduction is in complete harmony with the facts of observation since *para* alkyl derivatives always possess higher exaltations than the substances from which they are derived.[1]

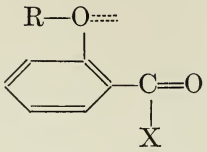
These relationships become much more complicated if two substituents in the benzene ring are unsaturated as is the case, for example, if the substituting radical is hydroxyl or alkoxyl instead of methyl. Even under these circumstances, however, *para* substitution products may be distinguished by the fact that they possess much greater powers of refraction and dispersion than the corresponding *ortho* and *meta* derivatives. Such an increase in optical exaltation may be readily understood by reference to the following formula:



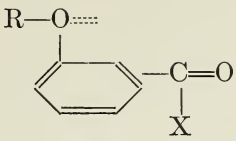
in which a continuous system of four conjugate linkages is represented.

[1] Ber., **45**, 2768 (1912).

In the case of *ortho* and *meta* derivatives

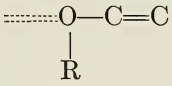


I.



II.

it is difficult to predict which will show the greater optical exaltation since the former possesses a continuous system of four pairs of conjugate double bonds while the latter contains two separate conjugate systems. It may be reasoned that *ortho* derivatives (I.) should show the stronger optical exaltations since a single conjugate of the type



is, so far as present observation shows, optically weak. This conclusion is in harmony with the fact that *o*-methoxy-benzophenone and *o*-methoxy-benzaldehyde are both characterized by strong optical exaltations. The experimental evidence is, however, too slight at the present time to allow of safe generalizations in regard to this or other similar phenomena.[1]

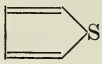
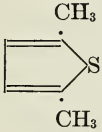
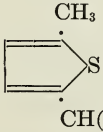
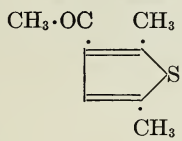
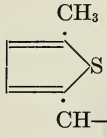
While it is remarkable that benzene shows no optical exaltation in spite of the presence of three pairs of conjugate double bonds, it is even more amazing that furane, thiophene, pyrrol, and cyclopentadiene, i.e.,

all show optical depressions. The fact that this statement includes cyclopentadiene eliminates the possibility of any explanation based upon the particular influence of the oxygen, sulphur, and nitrogen atoms. The cause for this anomalous condition must, therefore, be sought in the nature of the five-membered ring. Following the argument used in the case of benzene it may be assumed that the free affinity on the unsaturated atoms which normally would produce optical exaltation is in some way neutralized in maintaining the equilibrium of the ring. In the formation of these particular rings neutralization must be conceived to be so complete that in individual instances it actually produces the effect of optical depression.[2] The phenomenon is analogous

[1] Auwers, Annalen des Chemie, **408**, 212 (1915).

[2] Ber., **40**, 1157 (1907); **45**, 3077 (1912).

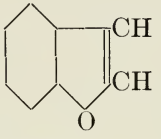
No.	Formula	$E\Sigma_\alpha$	$E\Sigma_D$	$E\Sigma_\beta - \Sigma_\alpha$ %	$E\Sigma_\gamma - \Sigma_\alpha$ %	Literature
1		−0.45	−0.47	+ 2	+ 4	Auwers, Ber., **45**,3078(1912).
2		−0.97	−1.10	− 8	+ 8	Nasini and Carrara, Gazz. chim.,**24**,1,278 (1894).
3		−0.39	−0.42	[+29][1]	+ 2	Gennari, Gazz. chim., **24**, I, 253 (1894).
4		−0.19	−0.19	+ 5	+ 5	Nasini and Carrara.
5		+0.56	+0.60	+43	+ 48	Gennari, and also Auwers, Ber., **44**, 3690 (1911).
6		+0.60	+0.72	[+56][1]	+ 46	Gennari.
7		+0.59	+0.63	+38	+ 42	Gennari.
8		+0.55	+0.59	+38	—	Gennari.
9		+0.59	+0.62	+34	—	Gennari.
10		+0.42	+0.43	—	+ 20	Brühl, Jour. prakt. Chemie. [2], **50**, 143 (1894).
11		+1.54	+1.69	+95	+110	Brühl, Annalen der Chemie, **235**, 7 (1886).

No.	Formula	$E\Sigma_\alpha$	$E\Sigma_D$	$E\Sigma_\beta - \Sigma_\alpha$ %	$E\Sigma_\gamma - \Sigma_\alpha$ %	Literature
12		−1.30	−1.31	− 3	− 4	Nasini and Scala, Rend. Acc. dei Linc., **1886**, 621; Knops, Annalen der Chemie, **248**, 204 (1888); Brühl, Zeitschr. physikal. Chemie, **22**, 392 (1897).
13		−0.44	−0.41	+ 8	+ 8	Nasini and Carrara.
14		—	−0.39	—	—	Grischkewitsch-Trochimowski, Chem. Centralbl., **1911**, II, 1239.
15		—	+0.25	—	—	Silberfarb, Chem. Centralbl., **1914**, I, 1663.
16		—	+0.99	—	—	Grischkewitsch-Trochimowski.

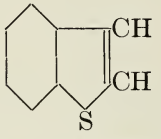
to that which is observed in the case of benzene since substitution of the hydrogen of the ring produces an analogous effect. Thus, for example, the introduction of an unsaturated group into substances containing a five-membered ring always lessens the optical depression of the substance and may even be so strong as to produce slight exaltation. This is demonstrated by a comparison of the results set forth in the preceding table. It is explicable on the assumption that, just as in the case of benzene, substitutions tend to disturb the equilibrium represented in

the neutralization of free affinity due to ring structure, and that this change to a condition where free affinity is actually operative in the molecule, corresponds to an increase in optical exaltation or, what is the same, a decrease in optical depression. The experimental material is at present so slight that it is difficult to make any generalizations as to the relationships which exist in five-membered rings. The results shown in the table on p. 312 would, however, seem to indicate that the appearance of a so-called *active* conjugation in such a compound, is attended by marked spectrochemical changes.

The data in the preceding table show that optical depression varies considerably in the case of different types of ring compounds. This would seem to indicate that while these substances are similar in constitution, their structure is by no means identical. The benzene derivatives of furane and thiophene

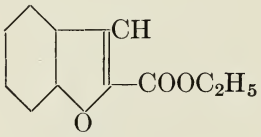


Cumarone

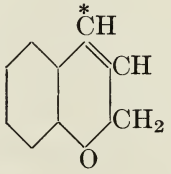


Thionaphthene

together with their various substitution products, show practically the same specific exaltation, and even the introduction of methyl or methoxy in the β-position produces no appreciable effect upon the spectrochemical relationships of these substances. This is true, for example, in the case of the esters of cumarilic acid:

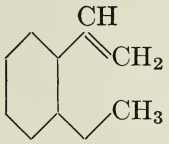


In the case of the chromenes, on the other hand,

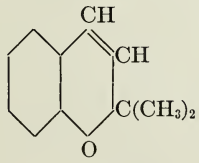
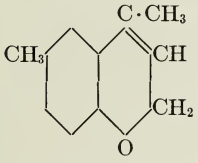
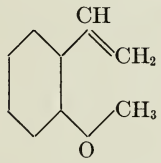
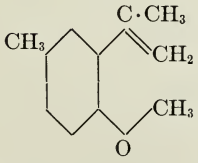


the substitution of methyl in the corresponding position (*) produces a very marked effect and is accompanied by a definite decrease in the

exaltation of the substance. This phenomenon has been observed, not only in connection with derivatives of chromene, but also in the case of the styroles



which closely resemble the chromenes in constitution in spite of the fact that they are open chain compounds.

No.	Formula	$E\Sigma_\alpha$	$E\Sigma_D$	$E\Sigma_\beta - \Sigma_\alpha$ %	$E\Sigma_\gamma - \Sigma_\alpha$ %
1		+1.15	+1.24	+54	+59
2		+0.86	+0.93	+47	+53
3		+1.12	+1.21	+57	+64
4		+0.78	+0.82	+32	+36

As a result of a general physical examination of the cyclo-hexanes, -hexenes, -hexanols, and -hexanons, Auwers [1] has discovered that the

[1] Annalen der Chemie, **410**, 287 (1915).

index of refraction increases in passing from a saturated to an unsaturated substance and decreases in passing from an alcohol to the corresponding ketone. A comparison of isomeric substances belonging to this series shows, moreover, that the molecular refraction is greater the further the side chains are from each other or from the double bond or from the substituent containing oxygen. The specific refractions of symmetrical compounds therefore usually show exaltations while in the case of unsymmetrical compounds they are either normal or depressed. The molecular dispersions of all saturated and unsaturated endocyclic compounds in this series are normal, and isomers show no optical differences within the limits of experimental error.[1]

Substances which contain systems of adjacent double bonds, as, for example, $-C{=}C{=}C-$, were said by Brühl to show no optical exaltation, but this statement has recently been questioned by K. von Auwers. Since the compounds which were selected for investigation by Brühl were open to certain objections, Auwers undertook a systematic study of certain of the allenes and ketenes with a view to determining the optical effect of so-called *cumulative* systems of the types $-C{=}C{=}C-$ and $-C{=}C{=}O$. As a result of this work[2] he was able to demonstrate that the refractions and dispersions of such compounds are not normal, but that they always show slight exaltations. The variation from normal in such cases is very small as compared with the exaltations which have been observed in the case of substances which contain *conjugated* systems. Indeed, in certain instances, as, for example, in the case of diphenyl and diethyl-ketene, they may even be so slight as to be negligible. The rule that a decrease in the degree of saturation of the atoms present in chemical compounds corresponds to an increase in their respective refractions and dispersions has been found to be of very general application. The effect of ring formation is of particular interest in this connection. Brühl originally believed that this effect was negligible, but a more exact investigation of the phenomenon has led to the discovery of an ever-increasing number of instances where ring formation is attended by marked changes in optical properties. This is especially true in cases where a condition of tension is assumed to result from the closing of the ring, as, for example, in trimethylene and tetramethylene derivatives where instances of optical anomalies have been observed frequently. It should be added, however, that ethylene oxide and its derivatives represent notable exceptions to this general rule.

K. von Auwers has recently made the spectrochemical effects of ring

[1] Annalen der Chemie, **410**, 330 (1915).
[2] Ber., **51**, 1124 (1918).

closure the subject of an extended investigation [1] and as a result of this work he has been able to formulate the following three rules. These rules apply particularly to the formation of benzene and its derivatives:

1. In all cases where a saturated chain closes to form a ring, the spectrochemical character of the original substance remains unchanged.

2. In cases where an unsaturated acyclic chain closes to form a ring, the optical effect of the unsaturated groups is weakened. This change is greater, the greater the degree of unsaturation of the original chain. In other words the optical effect of unsaturated linkages is less in closed than in open chains.

3. The presence of alkyl and other substituents in unsaturated chain compounds acts to retard ring formation.

It may be noted in passing that the spectrochemical behavior of saturated iso- and heterocyclic compounds, as well as of unsaturated iso-cyclic compounds, may be easily understood and may even be predicted on the basis of the above rules.

It is evident from even this brief survey of the subject that the experimental material available in this field is often very complex and very difficult of interpretation, and that the very slightest changes in the arrangements of the atoms within the molecule are reflected in the optical properties of the substance. Optical methods should, therefore, always be used in conjunction with chemical methods and never by themselves, and it should never be forgotten that all such data are based upon the laws of structural chemistry and that it, therefore, stands or falls with them. If these considerations are borne in mind, if sufficient care is taken in determining refractions and dispersions, and if comparative experiments are never neglected, spectrochemical methods will not only be found invaluable in elucidating fine points in regard to questions of structure, but will prove essentially helpful in developing the theory of structural organic chemistry.[2]

The relation of optical rotation to constitution may now be considered briefly. As is well known, substances which possess an asymmetric structure have the power to rotate the plane of polarized light. This property has been particularly associated with compounds which contain asymmetric carbon atoms, supposing, of course, that such atoms are not rendered inactive either by racemization or by intramolecular compensation. That a definite relation exists between the constitution of a given substance and its specific and molecular rotatory power has

[1] Annalen der Chemie, **415**, 98 (1917).

[2] Ber., **50**, 329 (1917); **51**, 1087, 1106 (1918); **52**, 584 (1919); Annalen der Chemie, **420**, 84 (1920); **421**, 1 (1920).

been fully demonstrated.[1] In some of the very early investigations undertaken in this field Guye was led to conclude that the rotatory power of a substance was materially influenced by the mass (or weight) of the substituents in union with an asymmetric carbon atom, but this was not conclusively proved, and further study tended to show that various other factors, such as homology, position isomerism, etc., affected rotation.[2] Thus, for example, in the case of isomeric substances possessing different rotations the variation was supposed to be due to the relative positions of the substituents in the molecule.

Soon after this Freundler discovered that the optical rotation of a substance is very much increased by the substitution of a phenyl group. This observation was confirmed by Tschugaeff,[3] who showed further that this influence is most felt in cases where the phenyl group occupies a position adjacent to the asymmetric carbon atom, and that the strength of this influence decreases in proportion to the distance separating the phenyl group from the asymmetric carbon atom.

The influence of unsaturated double bonds has since been made the subject of extended study by P. Walden,[4] A. Haller,[5] Hilditch,[6] H. Rupe [7] and others, and as the result of this study a number of rules which may be assumed to govern optical rotation have been formulated.[8] The list of substances which formed the basis of this investigation includes such compounds as the menthyl esters of a number of different acids, and derivatives of citronellal, carvoxime, myrtenol, and methylene-camphor. Before proceeding to a detailed consideration of this subject it will be of advantage to pause and review a few of the fundamental physical conceptions upon which the determination of optical activity is based.

The rotatory power of a substance is measured by means of an instrument called a polariscope. The angle of rotation for polarized

[1] Landolt "Das optische Drehungsvermögen organischer Substanzen," 2d Edition, 1896.

[2] Zeitschr. physikal. Chemie, **12**, 723 (1893); Bull. soc. chimie, **15**, 177 (1896); Annales Chimie et phys. **6**, 142 (1895); Compt. rend., **128**, 1370 (1895); Bull. soc. chimie, **11**, 316 (1894); Zeitschr. physikal. Chemie, **17**, 245 (1895).

[3] Ber., **31**, 1777 (1898).

[4] Zeitschr. physikal. Chemie, **20**, 569 (1896).

[5] Compt. rend., **128**, 1370; **129**, 1005 (1899).

[6] Jour. Chem. Soc., **93**, 1, 700, 1388, 1618 (1908); **95**, 331, 1570, 1579 (1909); **97**, 223, 1091, 2110 (1910); **99**, 218, 224 (1911).

[7] Annalen der Chemie, **327**, 157 (1903); **369**, 311 (1909); **373**, 121 (1910); **395**, 87, 136 (1913); **398**, 372 (1913); **402**, 149 (1914); **409**, 327 (1915); **414**, 99 (1917); **420**, 1 (1920).

[8] Trans. Faraday Soc., **10**, 1 (July, 1914).

light of definite wave lengths, represented by α_D for sodium light, depends upon the length of the rotatory column and also upon the temperature. In order to compare substances in cases where very unequal masses are contained in this column the observed rotation must in every case be divided by the specific gravity of the substance at the temperature at which the observation is taken. The specific rotation of an optically active substance may then be calculated by means of the expression

$$[\alpha]_D{}^t = \frac{\alpha_D{}^t}{l.d}$$

where $\alpha_D{}^t$ represents the observed angle of rotation of sodium light at the given temperature; l, the length of the column through which the light passes, and d, the density of the substance at the temperature at which the observation was made. The product of the specific rotation of a substance by its molecular weight represents its molecular rotatory power $[M]$, but since the values which are obtained in this way are apt to be large it is convenient to divide the molecular weight by 100, when the expression becomes

$$[M]^t{}_D = \frac{[\alpha]^t{}_D \cdot M}{100}$$

The values which represent the molecular rotations of different substances are frequently misleading for purposes of comparison because the numbers which represent the molecular weights are relatively so large that they serve to veil, rather than to accentuate, the observed small differences in rotation. Indeed H. Rupe [1] is of the opinion that a formula for determining optical rotations has yet to be devised which shall take into consideration the relative values which are expressed by means of molecular weights and not at the same time allow these to overshadow other factors of equal or greater importance in the equation.

In order to acquire the most complete knowledge which it is possible to obtain in regard to the relation between chemical constitution and optical activity it is necessary to determine the specific rotations of substances under the influence of polarized light of four different wave lengths, viz., the red C line, the yellow D line, the green E line, and the blue F line. From the data which are obtained in this way it is possible

[1] Annalen der Chemie, **420**, 21 (1920).

to calculate the specific rotatory dispersions of different compounds and by a comparison of these results to arrive at more or less definite conclusions as to molecular structure. Numerous instances of optical anomaly are met with in the field of rotation dispersions, but this phase of the subject must wait to be considered a little later in the discussion.

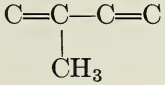
H. Rupe determined the optical rotations of a large number of menthol esters derived from both saturated and unsaturated acids and also of derivatives of the citronellals, carvoximes, and methylene-camphors. The immediate object of this investigation was to compare the rotatory powers of saturated groups with those of similar groups possessing different degrees of unsaturation. Another object was to determine the effect of substitution. In the latter case it was soon apparent that the introduction of methyl, or, in general, of alkyl groups in place of hydrogen was attended by insignificant changes in optical rotation and that even the presence of a number of such groups in the same part of the molecule failed to produce any appreciable effect. The introduction of unsaturated groups such as phenyl was, on the other hand, accompanied by marked changes in rotation. The most valuable results were obtained by comparing compounds which contain long aliphatic chains since in such cases the molecular weight of the substance was found to act as a kind of ballast. In general, the results showed that a condition of unsaturation generally corresponds to an increase in rotation and that this effect is relatively great when the unsaturated group is in direct union with the asymmetric carbon atom and may become negligible in cases where several other groups intervene. A conjugate system of double bonds has a more powerful influence upon rotation than two separate pairs of ethylene linkages.

The introduction of a phenyl group into a molecule containing an asymmetric carbon atom has a very pronounced effect upon rotation. This effect is greatest when the phenyl group occupies a position adjacent to the asymmetric atom, decreases gradually as the distance between the two becomes greater and finally, in certain instances, even swings over to the opposite sign. Rupe attempts to explain this phenomenon which has been observed in a great many cases by suggesting that the heavy phenyl group exercises greater leverage as the distance between it and the asymmetric carbon atom is increased.

The menthyl esters of sorbinic, dimethylsorbinic, and cinnamylacrylic acids were compared with the corresponding saturated compounds in an effort to determine the influence of conjugate systems upon rotation. The results of this investigation are given in the following table:

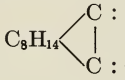
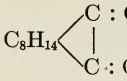
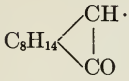
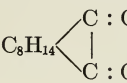
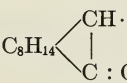
	$[\alpha_D]$
Menthyl ester of sorbinic acid and its reduction products:	
$CH_3 \cdot CH : CH \cdot CH : CH \cdot CO \cdot O \cdot C_{10}H_{19}$	88.53
$CH_3 \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	65.11
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	64.86
Menthyl ester of cinnamyl-acrylic acid and its reduction products:	
$C_6H_5 \cdot CH : CH \cdot CH : CH \cdot CO \cdot O \cdot C_{10}H_{19}$	75.14
$C_6H_5 \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	47.54
$C_6H_5 \cdot CH_2CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	33.86
Menthyl ester of dimethyl sorbinic acid and its reduction products:	
$CH_3 \cdot \underset{\cdot}{C}(CH_3) : CH \cdot \underset{\cdot}{C}(CH_3) : CH \cdot CO \cdot O \cdot C_{10}H_{19}$	59.80
$CH_3 \cdot \underset{\cdot}{CH}(CH_3) \cdot CH : \underset{\cdot}{C}(CH_3) \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	68.51
$CH_3 \cdot \underset{\cdot}{CH}(CH_3) \cdot CH_2 \cdot \underset{\cdot}{CH}(CH_3) \cdot CH_2 \cdot CO \cdot O \cdot C_{10}H_{19}$	57.38

It is apparent that a decrease in optical rotation accompanies the change from an unsaturated to a saturated compound in the case of the menthyl esters of sorbinic and of cinnamylacrylic acid. A comparison of the rotations of the esters of sorbinic and dimethylsorbinic acids shows that the substitution of methyl for ethylene hydrogen has a disturbing influence which is manifested by a pronounced decrease in rotation. This is analogous to the effect of methyl in the combination



which has been referred to in connection with the discussion of molecular refractions. In both cases the change in the optical properties which is produced by the substitution of methyl is marked.

In cases where a phenyl group forms part of a conjugate system which is in union with an asymmetric carbon atom the substance frequently shows an enormous increase in rotation as compared with a corresponding saturated compound. This is strikingly illustrated in the case of a number of substances, the rotations of which are given in the accompanying table:

	$[\alpha]_D$	M_D
I. Benzylidene camphor and its reduction products:		
	429.25	1020
	—	323
	—	248
II. Condensation production from citronellal and C_6H_5MgBr and its reduction products:		
$C_6H_{11}\cdot CH(CH_3)\cdot CH : CH\cdot C_6H_5$	63.24	135.4
$C_6H_{11}\cdot CH(CH_3)\cdot CH_2\cdot CH_2\cdot C_6H_5$	7.62	—
III. Cinnamylidene camphor and phenylpropyl camphor:		
	296.11	—
	66.35	—
IV. Optically active ester of cinnamic and hydrocinnamic acids:		
$C_6H_5\cdot CH : CH\cdot CO_2H$	76.95	220.8
$C_6H_5\cdot CH_2\cdot CH_2\cdot CO_2H$	58.48	168.4

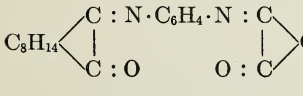
Here again the proximity of the unsaturated group to the asymmetric carbon atom represents an important factor in determining the optical rotation of a substance, as is apparent from a comparison of the following derivatives of citronellal:

	$[\alpha]_D$	M_D
$C_6H_{11}\cdot CH(CH_3)\cdot CH{=}CH\cdot C_6H_5$	63.24	135.4
$C_6H_{11}\cdot CH(CH_3)\cdot CH_2\cdot CH{=}CH\cdot C_6H_5$	3.33	7.6

In general it may be said that the action of any group which influences the optical rotatory power of a substance is a function of its distance from the asymmetric carbon atom.

A carbonyl group in conjunction with an ethylene group also tends to increase the optical rotation. Thus, according to Hilditch,[1] the influence of a carbonyl group is approximately as great as that of an ethylene group and the combination $CO \cdot CO \cdot O$ is just as effective as $C_6H_5 \cdot CO \cdot O$.

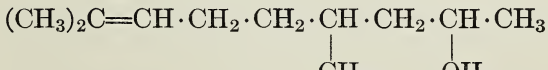
The unusually high values which are obtained in the case of *p*-phenylene-bisimino-camphor,

	$[\alpha]_D$	M_D
	1528	6100

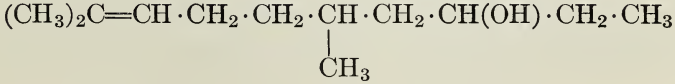
are very significant when noted in connection with the fact that this substance contains an unbroken chain of conjugations between carbon, nitrogen, and oxygen atoms.

The application of data, which have been obtained as the result of the measurement of rotations, to the determination of constitution is subject to the same limitations as have been described in connection with a discussion of molecular refractions and dispersions. The information which is gained in this way will always serve to support and amplify the knowledge of atomic relationships which have been acquired as the result of purely chemical investigations. The brief survey of Rupe's work in this field which has just been made demonstrates further that in highly competent hands the conclusions drawn from a comparative study of the rotatory power of different substances may also play an important role in the actual determination of constitution.

To add one more illustration to those which have been given, Rupe, Jäger, and others[2] have obtained two alcohols which correspond to the formulas:



and



[1] Jour. Chem. Soc., **99**, 224 (1911).
[2] Tran. Faraday Soc., **10**, 1 (1914).

by the action of methyl- and ethyl-magnesium bromide, respectively, upon citronellal. These alcohols both lose water, and in so doing pass over into two hydrocarbons which correspond to either the formulas I*a* or I*b* and II*a* or II*b*, respectively:

I*a*. $(CH_3)_2 : C{=}CH \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH{=}CH \cdot CH_3$

I*b*. $(CH_3)_2 : C{=}CH \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH{=}CH_2$

II*a*. $(CH_3)_2 : C{=}CH \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH{=}CH \cdot CH_2 \cdot CH_3$

II*b*. $(CH_3)_2C{=}CH \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH{=}CH \cdot CH_3$

It was observed that the hydrocarbon which was obtained by the use of $Mg(CH_3)Br$ showed a higher value for rotation, $[\alpha]_D = -10.30$, than the hydrocarbon which was obtained by the use of $Mg(C_2H_5)Br$ where $[\alpha]_D = -6.64$. On the basis of these measurements Rupe and Jäger concluded that the former compound possessed the constitution I*a* and the latter, the constitution II*b*, and the correctness of this deduction was confirmed by the decomposition of the substance under the action of ozone. In this way the definite relation which exists between the rotatory power and the constitution of a substance has again been established.

H. Rupe,[1] A. Akermann, and H. Kägi have recently obtained some very important results which are based upon the clever mathematico-physical analysis of A. Akermann [2] and which inaugurate a definite advance in a knowledge of the relationship which exists between the molecular structure and the optical rotation of organic compounds. Rupe [3] had discovered that the difference in dispersion represented by $[\alpha]_F - [\alpha]_C$ is constant for substances which belong to the same general class of chemical compounds. If this constant specific rotation-dis-

[1] Annalen der Chemie, **420**, 1 and 33 (1920).
[2] Dissertation, Basel, 1920.
[3] Annalen der Chemie, **409**, 336 (1915).

persion is regarded as a function of the wave length, it becomes possible to calculate the value for λ_α by means of the following equation [1]

$$\nu_\alpha^2=(\nu_C^2-\nu_D^2)\frac{[\alpha]_F-[\alpha]_C-[\alpha]_E}{[\alpha]_C-[\alpha]_D}+\nu_E^2\cdot\lambda_\alpha^2=\frac{1}{\nu^2},\ \lambda_\alpha=\frac{1}{\nu}$$

where ν represents the reciprocal wave length and λ_α, their so-called characteristic.

Since the values calculated for λ_α have been found to be fairly constant in the case of a great number of substances, it has become customary to compare the rotation-dispersions of different substances in terms of this constant. For example, if a substituting group produces no change in the value of λ_α, the behavior of the resulting compound is said to be *normal* with respect to dispersion, while if, on the other hand, the value of λ_α is altered by the introduction of a new group or by a difference in the configuration of the asymmetric complex, the dispersion of the resulting compound is said to be *anomalous*. In the latter case it is always assumed that constitutive changes have taken place within the molecule.

In order to determine the exact influence of different kinds of substituting groups upon the power of rotation of a given asymmetric complex, Akermann has deduced a law governing dispersions which is based upon a study of the behavior of substances possessing normal dispersions. The mathematical expression of this law not only includes variable wave lengths and deviations, but also contains one or more constants which are typical of the particular compound under investigation. Among the constants selected by Akermann are k_o, derived from the specific rotation; k_m, the so-called coefficient of optical activity; and λ_o^2, derived from the molecular rotation. The influence of the solvent upon rotation cannot, of course, be disregarded, but in the case of benzene, which was used exclusively by Rupe and his students, it was observed that the solvent had no effect upon the values λ_α and λ_o^2 within the limits of experimental error. The values representing the specific rotations were, however, affected by this solvent.

The relationships developed by Akermann may be expressed graphically in the form of a curve by plotting squares of the wave lengths as abscissa against the specific rotations for the different wave lengths as ordinates.[2] Differences in the form and position of the so-called rotation-dispersion curves which are obtained in this way serve to make changes in constitution instantly apparent and a comparison of a

[1] A. Hagenbach, Zeitschr. Physikal. Chemie, **89**, 581 (1915).

[2] Compare A. Hagenbach, Zeitschr. physikal. Chemie, **89**, 581 (1915); Rupe-Akermann, Annalen der Chemie, **420**, 5 (1920).

large number of such curves has demonstrated that the value for k_m is approximately constant in a large number of cases. For example, the introduction of saturated aliphatic groups or even of aromatic groups where the aromatic residue is separated by means of a methylene group from the asymmetric carbon atom produces no change in the value k_m. If, however, the aromatic residue is in direct union with the asymmetric carbon atom, a change involving an increase in the value of k_m occurs. A similar effect is brought about by the introduction of one or more ethylene or acetylene residues, although the difference is less marked in the latter than in the former case. The value of k_m is also materially changed if one or more groups which contain oxygen are introduced within the direct sphere of influence of the asymmetric carbon atom.

Rupe and Akermann assume that the coefficient of optical activity (k_m) is normal in all cases where the asymmetric complex contains only saturated hydrocarbon residues, none of which possesses additional asymmetric atoms. Normal and variable coefficients of optical activity must not, however, be confused with normal and anomalous rotation-dispersions, since substances possessing normal rotation-dispersions may show either normal or variable values for k_m.

The coefficient of optical activity is not influenced ordinarily by the number of atoms or groups which constitute the molecule, but is, on the other hand, dependent upon the space relationships of these atoms. If a substance possesses both a normal coefficient of optical activity and a normal rotation-dispersion, it may be assumed that this is conditioned by a certain definite arrangement of the individual atoms or groups of atoms with relation to each other and also with relation to the diameter of the molecule as a whole. Since changes in the relative space relationships of the atoms within the molecule correspond to differences in the molecular volumes of the substances, such changes can be readily followed by means of physical measurements. As is well known changes in molecular volume have been observed to accompany the substitution of ethylene and acetylene residues, of ketone and aldehyde groups, and the process of ring closure. Since, moreover, the coefficient of optical activity also depends upon changes in the space relationships of the atoms within the molecule, it is possible at the present time to predict with relatively great accuracy the effect of such changes upon the rotation-dispersion of asymmetric complexes. The various degrees of anomalous rotation-dispersion cannot be considered further at this time and the reader is, therefore, referred to Rupe's original paper for additional information.

[1] Annalen der Chemie, **420**, 57 (1920).

The relation between thermochemistry and constitution must now be considered, but here again the way must first be cleared by a few preliminary remarks. The internal energy of a body is that which is stored up within the individual molecules and is quite distinct from external energy whether this is kinetic or potential in character. In the case of an organic compound the internal energy bears a definite relation to the constitution of the molecule and is therefore different for different substances. It may be readily measured by the heat of combustion of any given compound since equal weights of the same substance always give the same quantity of heat when burned under the same conditions, while equal quantities of different substances give different heats. Even isomeric or polymeric bodies have different heats of combustion. This is true also of different allotropic forms of the same element, as, for example, graphite, carbon, and diamond.[1] These relationships were observed at a very early date and suitable calorimetric methods have since been developed and brought to a high degree of accuracy.[2] The heat of combustion is determined experimentally at constant pressure, but the figures obtained in this way must be corrected to constant volume, since in the process of burning changes in volume and in state of aggregation take place which involve change in energy. The heats of combustion of gases obtained by experiment may be used for comparative purposes. This is also true of the heats of substances in the liquid state, provided that the respective boiling points are approximately the same, since, under these conditions, differences in the molecular heats of vaporization will be negligible (Trouton's rule). From these values the respective heats of combustion in the gaseous state may be calculated by adding the molecular heats of evaporation of the respective substances. It is, however, difficult to draw accurate conclusions from a comparison of the heats of combustion of substances in the solid state. Great caution is needed in such cases since there are no general rules governing heats of fusion and these values vary considerably even for different modifications of the same element or compound.

The application of thermochemical data in the determination of

[1] Roth, Ber., **46**, 896 (1913).

[2] Berthelot "Thermochimie," Vol. IV; Stohmann, Jour. prakt. Chemie, **39**, 503 (1889); Lonquinine, "Hauptmethoden der Bestimmung der Verbrennungswärme," Berlin, 1897; E. Fischer, Sitzungsberichte der Berlin Akad. der Wissensch., **20**, 687 (1904); **24**, 129 (1908); Zeitschr. physikal. Chemie, **69**, 218 (1909); Auwers and Rothe, Annalen der Chemie, **373**, 239 (1910); Rothe, Annalen der Chemie, **373**, 249 (1910); also Annalen der Chemie, **385**, 102 (1911); **407**, 109, 112, 134, 145 (1915); Ber., **46**, 260 (1913); Jour. prakt. Chemie, **70**, 521 (1904); **96**, 123 (1917); **97**, 137 (1918).

constitution may be seen from the following example: the heat of combustion of 1 gram molecule of methane (16) has been found to be 211.9 Cal. The heats for carbon (as diamond) and for hydrogen have also been determined, and correspond, respectively, to the following values.

$$C + O_2 = CO_2 + 94.3 \text{ Cal.}$$

$$H_2 + O = H_2O + 67.5 \text{ Cal.}$$

The products of combustion in the case of methane are one molecule of CO_2 and two molecules of H_2O. From these facts it is now possible to calculate the heat of combustion of methane, viz.:

$$94.3 + 2 \times 67.5 = 229.8 \text{ Cal.}$$

This value exceeds that determined experimentally by 17.9 Cal. Since the first law of thermodynamics states that energy is never lost as heat, but merely transformed into some other equivalent, it is necessary to account in some way for the apparent disappearance of 17.9 Cal. This may be done by taking into account the following facts: the process by which CH_4 is transformed into $CO_2 + H_2O$ does not consist merely in the combination of C and O to form CO_2, and of H and O to form H_2O, but requires as a necessary preliminary to this action the decomposition of the methane molecule. The amount of work which must be done in order to sever the union between C and H to free these atoms is obviously equal to 17.9 Cal. and corresponds to the energy which is given off when C and H unite to form CH_4. In general it may be said that the difference between the heat of combustion of a given substance and the sum of the heats of combustion of the elements composing it represents the heat of formation of the compound. This latter value corrected to constant volume, and equal in the case of methane to 17.9 Cal., is frequently used in organic chemistry instead of the heat of combustion.

While the heat of formation of CH_4 is positive it often happens, especially in the case of unsaturated compounds, that this value is negative in character. For example, acetylene shows a difference between the heats of combustion as found (310.0 Cal.) and calculated (256.1 Cal.) of -53.9 Cal. In interpreting these facts it is necessary to assume not that energy is required to break the double bond between the carbon atoms, but that energy is actually set free during this process. Experience shows, in fact, that substances possessing double and triple bonds are more unstable and, therefore, more readily broken down than is the case with saturated compounds. This difference has been ex-

plained by supposing that a certain degree of tension is developed within the molecule by the union of the second pair of valencies of carbon to form the double bond, and that such an atomic arrangement must, therefore, be regarded as representing a definite amount of stored-up (i.e., potential) chemical energy.[1] If the equilibrium in a system of this kind is disturbed in any way this energy is set free. Thus in the process of burning it appears as heat and serves to increase the total heat of combustion of the substance.

It follows as a necessary corollary that in the formation of acetylene energy must be supplied from the outside. This is true, in general, of all so-called endothermic compounds as distinguished from exothermic compounds whose heat of formation is positive.

The illustrations serve to show that the heat of combustion of organic compounds is not merely additive, but is also constitutive in character. The numerical value of the additive and constitutive heats of various groups of atoms has been investigated by J. Thomsen, Welter, Horstmann, and others. Thomsen assumes that the four valencies of carbon are equivalent and that, at least in the case of hydrogen all four atoms are bound with equal strength to carbon. On this basis he argues that the amount of heat developed by the formation of one double bond is 15,465 Cal. less than in the formation of two single bonds between carbon atoms. In the same way Thomsen has calculated that in the union of two carbon atoms by means of a triple bond 43,922 Cal. less heat are developed than in the union of four carbon atoms by means of three single bonds. These figures are not, however, of wide application and even in their own limited field they have no general significance.

It might be supposed that the atomic heats of the elements could be calculated in the same way as in the case of refractions,—the values depending, of course, upon the form of combination of the atoms,—and that theoretical values could then be deduced for the heat of combustion of a substance, calculated upon the basis of its particular structure While the mass of experimental data which has been steadily accumulating for years undoubtedly tends definitely in this direction, yet, as Wrede[2] has recently pointed out, "any attempt which is made to calculate the heat of combustion of any substance from its constituents by means of a formula and by the use of empirical constants must be regarded as premature."

[1] Compare Nernst, Theoret. Chemie, 6th Edition, p. 328; also Stohmann and Schmidt, Zeitschr. physikal. Chemie, **21**, 314 (1896); Jour. prakt. Chemie, **53**, 345 (1896).

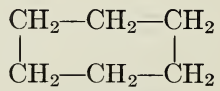
[2] See Thomsen, Zeitschr. anorg. Chemie, **40**, 185 (1904) and Auwers, Annalen der Chemie, **385**, 103 and following (1911).

But while it is as yet impossible to calculate the heat of combustion or the heat of formation of a substance from the sum of the additive and constitutive heats of its atoms in the same way as in the case of refraction and dispersion, it is, nevertheless, possible to apply thermochemical data to the determination of constitution. These relationships have recently been the subject of systematic investigation by E. Fischer and Wrede, as well as by Auwers and Roth, and a number of important conclusions have been reached.

It was at first supposed that in the case of an homologous series the respective heats of combustion differed always by a constant which corresponded to CH_2, but it has since been found that these values are only approximately constant and that they frequently vary considerably from the mean. Isomeric compounds belonging to the same general class have almost exactly the same heats of combustion, but here again small variations have been observed. For example, primary alcohols have greater heats of combustion than secondary and tertiary alcohols, and substituted malonic acids have higher heats than the corresponding succinic acids. In instances where one isomer represents a stable, the other an unstable modification as in the case of fumaric and maleic acids it has been found that the labile form possesses the greater heat of combustion.[1] Straight chain unsaturated compounds show greater heats than isomeric ring compounds. This is true, for example, in the case of the following substances:

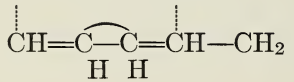
$CH_3(CH_2)_3—CH=CH_2$

Hexene



Cyclohexane

Important results have been obtained by the application of thermochemical data to the study of unsaturated compounds. The calorimetric relationships between benzene and hydrobenzene have already been referred to and there are many other instances of theoretical conceptions which have been confirmed in this way. Thus, for example, in formulating his theory of partial valencies, Thiele assumed that of two unsaturated systems



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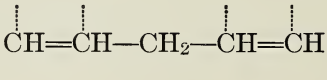
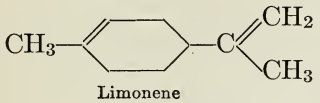


the latter would have the greater heat of combustion since it was to be regarded as the more unsaturated. It is interesting to note that this assumption has been confirmed as the result of recent investigations by

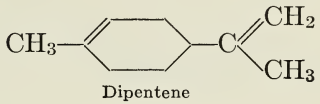
[1] Compare Roth, Ber., **46**, 260, 326 (1913).

Auwers and Roth. These authorities in co-operation with Eisenlohr have also examined these substances spectrographically and have found that a remarkable analogy exists between optical and thermal properties.

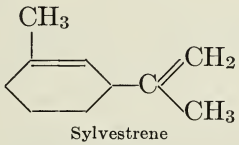
That conjugate systems in general represent less chemical energy and, therefore, possess greater stability and lower heats of combustion than other systems of double bonds has been demonstrated very clearly by an examination of the terpenes. For example, such substances as



Limonene

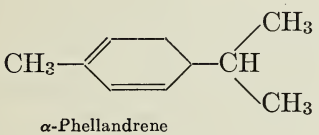


Dipentene

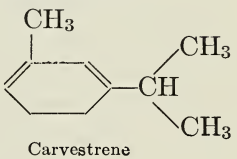


Sylvestrene

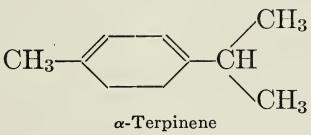
have greater heats of combustion than such substances as



α-Phellandrene



Carvestrene



α-Terpinene

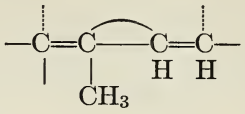
and this is ascribed to the fact that members of the second series possess conjugate systems of double bonds. A similar relation holds in the styrole series,[1] although the differences are not so striking here as in the case of the terpenes.

Since substances containing conjugate systems have been found to have low heats of combustion and at the same time to show optical exaltation it has been possible by taking the two sets of facts in conjunction to settle certain doubtful questions in regard to constitution. For example, a substance is usually assumed to possess a conjugate system of double bonds if it exhibits both optical exaltation and a low heat of combustion. It is, therefore, advisable to determine both sets of physical constants in all cases where this is at all practicable.

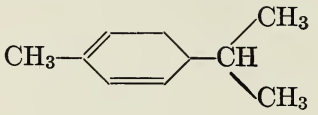
In conclusion it may be added that another analogy between thermal and optical properties is to be observed in the effect of the substitution of

[1] Annalen der Chemie, **373**, 287 (1910).

hydrogen which is attached to the central carbon atoms of a conjugate system. It has already been pointed out that substitution in this position, as represented in the combination



often completely neutralizes the optical exaltation of the system. For example, α-phellandrene



exhibits optical disturbances of this character and also shows a corresponding decrease in the anomaly of its heat of combustion.

In studying the heats of combustion of ring compounds it has been found that three- and four-membered rings give relatively high values when compared with five- and six-membered rings. The facts of observation are, therefore, in general agreement with the assumption of Baeyer's tension theory. That the energy relations between ring compounds are not all so simple as Baeyer's theory would suppose is obvious from a consideration of the following facts. In investigating the heats of combustion of tetramethylene derivatives Stohmann found that the respective heats of these substances are greater than those of the corresponding trimethylene derivatives. These observations have recently been confirmed by Roth and Ostling who, as a result of very careful investigation, have discovered that ring systems, exclusive of the presence of double bonds, may be arranged in the order of their energy content as follows:

$$4>3>7>6>5$$

Marked asymmetry in the arrangement of the substituents in the molecule seems to increase the energy of the compound, and the presence of a double bond between the atoms constituting the ring has in general the same effect.

It may be said in conclusion that since the heats of combustion of relatively few substances have as yet been determined, it may be anticipated that the further comparison of thermal and optical properties will lead to results of the utmost importance in developing the structural theory of organic chemistry.

The relation of other physical constants, such as magnetic rotation [1] and conductivity,[2] to constitution cannot be discussed at this point since their detailed consideration would require more space than could with propriety be allowed within the limits of the present volume.

[1] See Perkin, Jour. Chem. Soc., **55**, 680 (1889); Zeitschr. physikal. Chemie, **21**, 451, 561 (1896); **27**, 447 (1898).

[2] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Leipzig.

CHAPTER XIV

THE THEORETICAL SPECULATIONS OF JOHN ULRIC NEF

In 1890 the American chemist J. U. Nef [1] brought forward original views which, supported as they were by experimental data, attacked the very root and fiber of the theories in regard to organic reactions which were current at that time. Nef not only objected to the prevailing views in regard to tautomerism, but even refused to recognize the new progressive achievements in that field which dealt with the stereochemistry of nitrogen. Above all, he denied two fundamental assumptions which had been and still were invaluable to organic chemists, namely, the assumption of the constant quadrivalence of carbon in organic combinations and the assumption of substitution or *metalepsis* as representing the mechanism of a great number of chemical reactions. Nef attacked the prevailing conception in regard to metalepsis most energetically and maintained that it and the other hypotheses brought forward in connection with it during a period of thirty years were not only illogical, but were responsible for the confusion of thought which then reigned in organic chemistry. Nef represented in speech the purest type of a revolutionist and the question naturally arises as to whether his conclusions were sound and in the end better than the conceptions advanced by earlier investigators. In answer to this question it may be said that whether his views are accepted or not, it cannot be denied that he was a conscientious and close student of his science, that he honestly endeavored to present sound theory, and that, being an excellent experimentalist, he was able to support his speculations with original and reliable data. With these introductory remarks Nef's speculations will now be presented to the reader in the form in which he himself has presented them in an excellent paper which was published by the Journal of the American Chemical Society in 1904,[2] and which, through the courtesy of the publishers, has been incorporated in the present volume. A critical discussion of the funda-

[1] Annalen der Chemie,, **258**, 261 (1890); **266**, 52 (1891); **270**, 267 (1892); **280**, 291 (1894); **287**, 265 (1895); **298**, 202 (1897); **309**, 126 (1899); **318**, 1, 137 (1901); **335**, 191, 247 (1904); **357**, 214 (1907).

[2] Jour. Am. Chem. Soc., **26**, 1549 (1904); compare also **30**, 645 (1908).

mental conceptions embodied in this paper as well as a consideration of later developments from it, will be reserved for consideration in the next chapter.

The progress of organic chemistry since 1858 is due chiefly to the development of a few very simple ideas concerning the valence of the elements, ideas which were first clearly and fully presented at the time of Kekulé.

Hydrogen, oxygen, and nitrogen are the elements which most frequently combine with carbon to form the so-called organic compounds. Since the compounds of one atom of oxygen, nitrogen, or carbon with hydrogen possess the empirical formulas, $O{=}H_2$, $N{\equiv}H_3$, $C{\equiv}H_4$, the conception naturally presents itself that the capacity of the various elements for holding hydrogen atoms varies. Oxygen is capable of holding two such atoms, nitrogen holds three, and carbon four atoms of hydrogen. Therefore, we assume, taking hydrogen as our unit, that the valence of the element oxygen is two, $-O-$; of nitrogen, three, $-\overset{|}{N}-$; and of carbon, four, $-\overset{|}{\underset{|}{C}}-$. Without going into much detail concerning the nature of the valence, or what is the same thing concerning the nature of the forces inherent in our atoms, we assume briefly that every atom of an element possesses one, two, three, four, or more such units of force and we call the element univalent, bivalent, trivalent, quadrivalent, etc., according to the number of such units it possesses. It is by virtue of the existence of these units of force that the compounds made up of the same or of various elementary atoms exist. We assume that in such a molecular compound the atoms are bound one to another in a definite way by means of their affinity units.

Since the development of these ideas concerning the valence of the elements there has been a great deal of work carried on with the object of determining whether the valence of an element is constant or whether it may vary; the majority of chemists are now convinced that it may vary.

The valence of nitrogen may be three or five. The valence of hydrogen, oxygen, and carbon, on the other hand, have, until recently, been assumed always to remain constant, i.e., one, two, and four, respectively.

Since the complexity, and the very great variety and number of existing compounds containing carbon are unquestionably to be attributed to the peculiar nature of the forces inherent in the carbon atom, let us consider a little more in detail what hypotheses we make in our present

system of carbon chemistry concerning this element. We assume first that the valence of the carbon atom is always four; second, that the four valences or affinity units of the carbon atom are equivalent; third, that they are distributed in space in three dimensions and act in the direction of the axes of a tetrahedron; fourth, that the carbon atoms can unite with one another by means of one, two, or three affinity units to form what we usually call chains. These chains may be open, or closed rings or cycles. The number of carbon atoms thus bound to one another may be exceedingly large. The closed chains usually contain three, four, five, six, or seven carbon atoms in the ring. We may have in these chains, whether open or closed, some of the carbon atoms replaced by oxygen, nitrogen, sulphur, or other elements. If now we unite the extra valences of each carbon or other atom—i.e., those affinity units which are not necessary for binding the atoms together in chains—with other atoms or radicals, it is at once evident that we can represent, theoretically, by so-called graphical formulas, molecules of great complexity.

It is also at once obvious that with a small number of atoms it must be possible to construct a relatively large number of aggregates which differ from one another simply in the way the atoms are bound together. In 1884, for instance, fifty-five totally different substances of the empirical formula $C_9H_{10}O_3$ were actually known. We call them isomers.

One of the chief problems of organic chemistry, since 1858, has been to determine on the basis of these ideas of valence the " constitution " of the carbon compounds. We determine by methods which are called synthetic, as well as by an exhaustive study of the reactions of a given compound, what may be called the " architecture " of its molecule, i.e., we determine how the various atoms of carbon, nitrogen, oxygen, hydrogen, etc., of which the substance may be composed are joined together by virtue of of their affinity units. How much has been accomplished on the basis of these ideas during the past forty-six years and how beautifully and simply all the facts known with regard to the almost countless carbon compounds are thus explained, only those can fully appreciate who have a detailed knowledge of the subject. Notwithstanding the large number of workers in the field, it has often required more than a decade of work to determine the molecular architecture of one single carbon compound, and the question at times seriously presents itself whether we must not reach our limitations in this respect.

In any case, one point is deserving of especial emphasis: this idea of structure which has been applied chiefly to molecules containing the

element carbon attributes to them a rigidity which is improbable from a purely dynamic standpoint.

The present system of organic chemistry is thus founded upon the assumption that the valence of all the atoms of carbon, wherever found, remains invariably four. In the earlier part of the last century many attempts were made to isolate the hydrocarbon methylene, CH_2, which must contain bivalent carbon. Dumas and Peligot tried to obtain this substance from methyl alcohol, $H \cdot CH_2 \cdot OH$, by loss of water. Perrot tried to isolate it from methyl chloride, $H \cdot CH_2 \cdot Cl$, by dissociation into methylene and hydrogen chloride at a high temperature. Berthelot, Butlerow, Wurtz, and Kolbe also made many fruitless attempts in this direction. As a final result of these repeated and negative efforts chemists finally became convinced that compounds containing bivalent carbon could not be isolated and the conclusion, therefore, that carbon was one of the few elements possessing a constant valence became very general.

There has, however, long existed one very simple compound of carbon which does not adjust itself to this system—namely, the inactive and poisonous carbon monoxide. If we assume the valence of oxygen as two, then we have here simply a derivative of methylene in which the two hydrogen atoms are substituted by oxygen, C=O. To be sure, there were many chemists who preferred to consider the valence of carbon in carbon monoxide as four, thus making the valence of oxygen four, C≡O, and when we bear in mind that the other members of the oxygen group, sulphur, selenium, and tellurium, exist as di-, tetra-, and hexavalent atoms there is some justification for this interpretation. To me, personally, however, it seems in the highest degree improbable that two atoms should be thus bound to each other by four affinity units.

About fourteen years ago a series of systematic experiments was undertaken with the object of ascertaining whether carbon can exist in a bivalent condition. The experiments have established this point in a most decisive manner; we have now quite an array of substances which contain bivalent carbon.

Furthermore, it has been possible to prove, from the experience gained in their study, that methylene chemistry plays an important rôle in many of the simplest reactions of organic chemistry, reactions which have hitherto been explained on the basis of substitution.

At the time when these experiments were undertaken there existed, besides carbon monoxide, several substances which might contain bivalent carbon—namely, prussic acid and its salts, the cyanides, HN=C and MN=C. Also the so-called carbylamines, RN=C,

discovered in 1866 by Gautier. These substances were, therefore, exhaustively studied in order to establish rigidity, by experiment, whether bivalent carbon was present or absent. The presence of *dyad* carbon in these compounds having been established and its properties thus being known, the problem then presenting itself was the isolation of methylene and its homologues.

You are probably all aware that Gay-Lussac established, in 1815, the existence of a radical, composed of one atom of carbon and one of nitrogen, in prussic acid and the cyanides. This radical, cyanogen, plays in its compounds a rôle similar to that of the elements of the halogen group. In 1832 Pelouse discovered the alkylcyanides, RC≡N, by treating potassium cyanide with alkyliodides or with alkyl potassium sulphates;

$$KCN+RI \text{ or } ROSO_2OK \rightarrow R-C\equiv N+KI \text{ or } KOSO_2OK,$$

an apparent double decomposition reaction by which we obtain a compound in which the radical $R(C_nH_{2n+1})$ is joined to the cyanogen group by means of carbon. The alkylcyanides thus obtained are neutral, pleasant smelling, harmless liquids resembling ether, chloroform, and the alkylhaloids, RCl, RBr, and RI.

In 1866 Gautier discovered a new class of organic compounds by treating cyanide of silver with alkyliodide,

$$RI+Ag(NC) \rightarrow AgI+RN{=}C,$$

a reaction which is apparently a double decomposition reaction. They are isomeric, not identical, with the alkylcyanides of Pelouse. He called them the carbylamines or isonitriles and proved that the alkyl group is bound to the cyanogen radical by means of nitrogen, RN=C or RN≡C.

It thus became evident that we must distinguish between two cyanogen radicals—namely, one which in its compounds, is bound to alkyl-hydrogen or metal by means of carbon, RC≡N, HC≡N, MC≡N, and another which is joined to these elements, or groups by means of nitrogen, RN=C, HN=C, MN=C. We may call the former radical cyanogen, —C≡N, and the latter isocyanogen, —N=C or —N≡C; these radicals may, obviously, combine with each other to form three isomers of the empirical formula, C_2N_2. The substances discovered by Gautier, the alkylisocyanides, RN=C or RN≡C, have properties strikingly different from those of their isomers—the alkylcyanides, RC≡N, of Pelouse.

They are poisonous, nauseating compounds which affect the throat

like prussic acid and color the blood intensely red; they produce violent headaches and vomiting. Their odor is most pronounced and persistent. Hofmann, who, in 1868, discovered another method for making them from primary amines, chloroform, and caustic potash,

$$RNH_2+3KOH+CHCl_3 \rightarrow RN{=}C+3KCl+3H_2O,$$

found it impossible to work with them except for very short periods.

An exhaustive study of the reactions of these alkyl isocyanides, carried out in 1891–2, led to the definite conclusion that they contain a *dyad* carbon atom—i.e., they possess the constitution represented by the formula RN=C; the other possible formula with quadrivalent carbon and quinquivalent nitrogen, RN≡C, is excluded by the facts.

The alkylisocyanides belong to the vast category of unsaturated compounds whose chemistry will be briefly discussed from a perfectly general standpoint below; they manifest their great chemical activity especially by absorbing other substances, forming new molecules in which the valence of carbon has changed from two to four. Such reactions we call additive. Two molecules simply unite to form one new molecule—the addition product.

A molecule containing an unsaturated carbon atom—i.e., one with two of its valences latent or polarized, RN=C, cannot, *per se*, show any chemical activity whatever.

This is also true of a system containing a pair of doubly or triply bound carbon atoms, ethylene, $CH_2{=}CH_2$, and acetylene, HC≡CH; and finally of a saturated system which we may represent by a paraffine, C_nH_{2n+2}, for instance, marsh gas, CH_4.

All these substances manifest chemical activity simply because they are, to a greater or less degree, in a dissociated, or what may be called an active condition.

A given quantity of alkyl isocyanide contains an extremely small per cent of molecules with two free affinity units, RN=C<; these are in dynamic equilibrium with the absolutely inert molecules, RN=C. That this percentage varies with the nature and mass of R is shown by the fact that various alkylated and arylated isocyanides manifest different degrees of chemical activity. Carbon monoxide possesses relatively a smaller number of such active particles, O=C<, and consequently is a comparatively inert substance, since the speed of addition reactions shown by unsaturated compounds must naturally be directly in proportion to the per cent of active molecules present. A similar conception obviously explains the relative differences in reactivity shown by the various members of the olefine and acetylene

series. Marsh gas, a saturated system, reacts with other substances because it is partially dissociated as follows:

$$CH_4 \rightleftarrows CH_3\text{-----}H \quad \text{and} \quad CH_2\text{::::::}2H$$

From this point of view chemical action depends entirely upon dissociation processes. The reactions often proceed with very great slowness because the percentage of dissociation is extremely low, possibly 0.1 to 0.001 per cent, or even less.

Turning now to a consideration of the reactions of alkyl isocyanides, the substances which are absorbed by the unsaturated carbon atom present in the isonitriles are the following:

I. "Halogens" (chlorine, bromine, iodine; speed of reaction in the order named),

$$RN{=}C{<}+\underset{|}{X}{=}\underset{|}{X} \rightarrow RN{=}C\begin{matrix}X\\ \|\\ X\end{matrix} \rightarrow RN{=}C\begin{matrix}X\\ X\end{matrix}$$

The reactions, expecially those with chlorine and bromine, take place with great evolution of heat at $-20°$.

II. "Acid Chlorides," such as RCOCl, $ClOC_2H_5$, ClCOCl, ClCN, ClCOOR form the addition products.

$$RN{=}C\begin{matrix}Cl\\ COR,\end{matrix} \quad RN{=}C\begin{matrix}Cl\\ C:O,\\ Cl\end{matrix} \text{ etc.}$$

A hyphen denotes the point where the compounds are partially dissociated and consequently absorbed. These reactions, especially those with phosgene and ethyl hypochlorite, take place with great violence at $-20°$.

III. "Oxygen and Sulphur," form isocyanates and mustard oils, RN=C=O and RN=C=S. Methylisocyanide unites directly at its boiling-point, 58°, with the oxygen of the air. The dry oxides of silver and mercury are reduced to metals with violence at 40°, alkyl isocyanate being first formed. This shows the great affinity of bivalent carbon for oxygen.

IV. "Primary Amines and Hydroxylamine,"

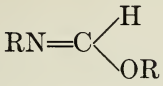
$$RN{=}C{<}+H{-}NHR \quad \text{or} \quad H{-}NHOH \rightarrow RN:C\begin{matrix}H\\ NHR\end{matrix}$$

or

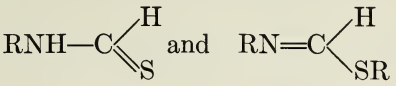
$$RN{=}C\begin{matrix}H\\ NHOH\end{matrix}$$

give amidines and oxyamidines.

V. "Alcohols," in the presence of an alkali, are absorbed, giving imido ethers,



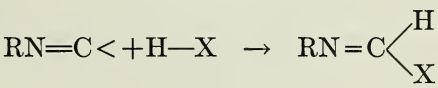
VI. "Hydrogen, Sulphide and Mercaptans," give readily at 100° the addition products

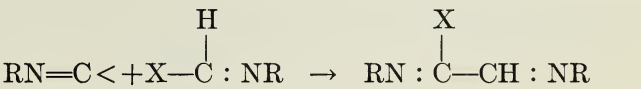


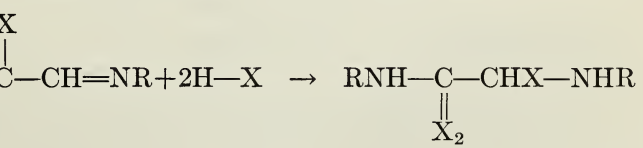
VII. "Acids." Aqueous mineral acids act with great violence on the isonitriles, giving primary amines and formic acid,

$$RN{=}C{<}+2H_2O \rightarrow RNH_2+H\cdot COOH$$

In the absence of water and on diluting the alkylisocyanides with absolute ether, perfectly dry halogen hydride causes the separation of white hygroscopic salt-like substances of the empirical formula 2RNC, 3HX(X=Cl, Br, or I). For this reason Gautier, as well as Hofmann, supposed the isonitriles to be basic compounds—i.e., substances behaving like ammonia—hence, the name carbylamine was given them by Gautier. Further study has shown, however, that this conclusion was erroneous. The isonitriles are entirely devoid of basic properties; the great violence with which they react with halogen hydrides is due to the presence of unsaturated carbon. The reaction probably takes place as follows:

I. 

II. 

III. 

Reversibilty of the Reactions.—The most striking property of these addition products of the isonitriles, RN : C$\langle^{X}_{Y}$, is their low point of dissociation—i.e., the carbon atom which has absorbed the X—Y thus becoming quadrivalent is unable to hold X—Y above certain

temperature limits. There is consequently in every case a temperature varying with the nature and mass of X and Y, as well as with the nature and mass of the groups bound to the other two affinity units of carbon, at which the carbon atom becomes spontaneously *dyad* and is unable to remain in a quadrivalent condition; it was subsequently possible to prove that this is a perfectly general property of this atom.

All the addition products under discussion are partially dissociated,

$$RN : C\begin{matrix}X\\Y\end{matrix} \rightleftarrows RN{=}C{<}{+}X{-}Y$$

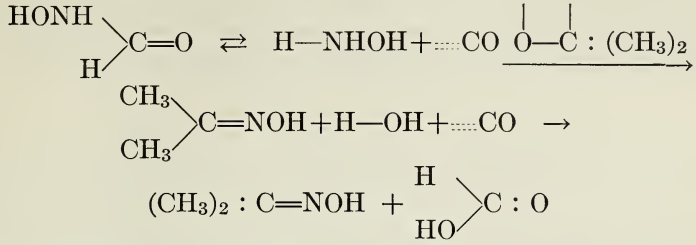
the dissociation increasing as the temperature is raised—in other words, the valence of carbon at temperatures below the dissociation point is an equilibrium phenomenon; dynamic equilibrium exists between bivalent and quadrivalent carbon.

The point of complete dissociation of the various addition products of the isonitriles has not yet been accurately determined in every case. The following data with reference to the dissociation points of carbon monoxide addition products are of interest and therefore used for illustration in this connection:

		Dissociation Point
Formaldehyde,	$O : C{<}H_2$	600°
Formamide,	$O{=}C\begin{matrix}H\\NH_2\end{matrix}$	250° (about)
Formic acid,	$O{=}C\begin{matrix}H\\OH\end{matrix}$	169°
Formhydroxamic acid,	$O{=}C\begin{matrix}H\\NHOH\end{matrix}$	85°
Formylchloride,	$O : C\begin{matrix}H\\Cl\end{matrix}$	−20° (below)

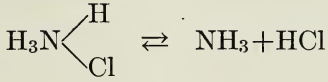
Since these substances containing quadrivalent carbon decompose spontaneously into carbon monoxide, i.e., cannot exist in the quadrivalent condition at temperatures above those indicated, it is self-evident that at lower temperatures the addition products must be partially dissociated and that in the future we must be able to determine, in each case with absolute accuracy, the percentage of dissociation at any temperature. A striking experiment with formhydroxamic acid, with a dissociation point of 85°, proves the correctness of this conclusion;

on allowing this crystalline substance to stand at 20° in acetone solution the following reaction takes place quantitatively:



In a similar manner we can prove that the isonitrile addition products, many of which have definite boiling-points and are quite stable, are partially dissociated at ordinary temperatures. Thus the addition products with halogens, $RN{=}C\langle^{X}_{X}$, are all converted back quantitatively into the alkylisocyanides by treatment with finely divided metals, zinc dust, or sodium, which simply abstract the free halogen.

Many of the acylhalide addition products dissociate spontaneously into the components on distillation; these phenomena are perfectly analogous to the dissociation of dry ammonium chloride,

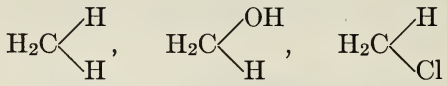


For this reason the majority of the addition products of the isonitriles can be kept only for a short time; this property rendered futile many attempts to isolate definite addition products. The continual dissociation of such products sets free active or dissociated alkylisocyanide particles, and these slowly condense with one another,

giving rise to the so-called alkylisocyanide resins (non-reversible) or products whose molecular weight has not yet been determined and which are perfectly analogous to azulmic or polymerized prussic acid. Consequently, in carrying out an addition reaction with an isonitrile, especially if it requires much time or a temperature above 20°, large quantities of these resinous polymers are formed from which it is possible to isolate the addition product only with great difficulty. Many of the isonitriles themselves, even when perfectly pure, undergo rapid polymerization to resins so that they can be kept only for a very short time. Phenylisocyanide, $C_6H_5N{=}C$, is the most striking instance, as

it changes in a few minutes from a colorless to a dark-blue liquid and in a few days condenses to a dark-brown resin.

Have we not here a possible explanation of the fact that it is impossible to isolate methylene and a large number of its derivatives, although marsh gas, methyl alcohol, and chloride of methyl,



each contain a relatively small percentage of active methylene particles at ordinary temperatures?

The presence of bivalent carbon in the alkylisocyanides having been established, the next question presenting itself was whether prussic acid and its salts contain the cyanogen or the isocyanogen radical. In the latter case, HN : C, MN : C, these substances must be analogous to Gautier's isonitriles. It had hitherto been considered as established, but without sufficient evidence, that prussic acid and the cyanides were cyanogen compounds analogous to the nitriles of Pelouse.

When one considers the physical and physiological properties of prussic acid (boiling-point, 25°; sp. gr., 0.70; a violent poison) and contrasts these with the corresponding properties of methylcyanide (boiling-point, 81°; sp. gr., 0.81; sweet-smelling, harmless oil) and of methylisocyanide (boiling-point, 58°; sp. gr., 1.75; a poison) one at once comes to the conclusion that prussic acid, as well as its salts, must belong to the isocyanogen compounds and consequently must contain bivalent carbon.

An exhaustive study of prussic acid and the cyanides establishes this sharply, especially in the case of the salts, from a chemical standpoint. The relation of fulminic acid to prussic acid corroborated the evidence.

You are all familiar with fulminate of mercury—a substance which is made on a commercial scale and used for explosives. It was discovered in 1800 by Howard, and analyzed in 1824 by Liebig in Gay-Lussac's laboratory. We obtain it by dissolving mercury in concentrated nitric acid and adding the resulting solution to ordinary alcohol. It has the empirical formula $HgC_2N_2O_2$, and, being obtained from ethyl alcohol, CH_3CH_2OH, fulminic acid was supposed to have two carbon atoms in its molecule, $H_2C_2N_2O_2$. The constitution of this substance was, for a long time, a great puzzle to chemists. That we have here a substance very closely related to prussic acid was discovered by accident. In working with the mercury salt of isonitro-

methane it was found that this compound is spontaneously converted at 0° into fulminate of mercury, according to the equation,

$$H_2C{=}NOhg \rightarrow \begin{matrix} H \\ HO \end{matrix}\!\!>\!C{=}NOhg \rightarrow H_2O{+}C{=}NOhg$$

This synthesis led directly to the conclusion that fulminate of mercury possesses a constitution entirely analogous to cyanide of mercury, C=Nhg, i.e., that it contains the isocyanogen radical with bivalent carbon. A further study of the fulminate established this point with precision. Especially striking is the behavior of fulminates towards dilute acids. Liebig and Gay-Lussac stated, in 1824, judging from the odor, that fulminate of silver gives prussic acid with dilute hydrochloric acid. A more careful study of this reaction, in 1894, proved that not a trace of prussic acid, but a substance, formyl chloride oxime, $\begin{matrix} H \\ Cl \end{matrix}\!\!>\!C{=}NOH$, is formed, which possesses the following remarkable properties: long needles, clear as glass, which decompose and explode with violence at 20°; extremely volatile even at 0° and having an odor similar to prussic acid, which is obviously due to a partial dissociation into fulminic acid. Aqueous silver nitrate converts it quantitatively into chloride and fulminate of silver,

$$\begin{matrix} H \\ Cl \end{matrix}\!\!>\!C{=}NOH{+}2AgNO_3 \rightarrow AgON : C{+}AgCl{+}2HNO_3$$

Up to 1897 the presence of bivalent carbon had been established in the following compounds: 1, carbon monoxide, C : O; 2, the alkyl and aryl isocyanides, RN : C; 3, prussic acid and the cyanides, NH : C, MN=C; 4, fulminic acid and the fulminates, (HO)N : C, MON=C. 2, 3, and 4 are all compounds containing the isocyanogen radical. In 1897 the presence of bivalent carbon was established in a series of nitrogen-free carbon compounds obtained from acetylene. They are the mono- and di-halogen substituted acetylidenes,

$$\begin{matrix} X \\ H \end{matrix}\!\!>\!C{=}C \quad \text{and} \quad \begin{matrix} X \\ X \end{matrix}\!\!>\!C{=}C(X{=}Cl, Br \text{ or } I)$$

The corresponding members of the acetylene series, XC≡CH and XC≡CX, do not exist, although we have substances like $CH_3C{\equiv}CI$,

$C_6H_5C{\equiv}C{-}X$, whose properties are in marked contrast to those of the acetylidene derivatives.

Diiodacetylidene, which possesses an odor deceptively like that of the isonitriles, dissociates at 100° with violence into iodine and diatomic carbon,

$$I_2C{=}C \rightarrow I_2 + C{=}C$$

the latter cannot be isolated as such, but polymerizes explosively to graphite and amorphous carbon. The mono- and dihalogen substituted acetylidenes are all poisonous and spontaneously combustible compounds, possessing, therefore, like methylisocyanide, a marked affinity for oxygen.

Up to the present time it has not been possible to isolate compounds containing bivalent carbon, other than those mentioned above. We are, however, now in a position to explain clearly why we cannot hope, by methods now known, to isolate methylene and its homologues as such, although these substances play a great rôle in many of the fundamental reactions of organic chemistry.

In order to approach this point more intelligently let us first consider the properties of unsaturated compounds in general, their possibility of existence, etc.

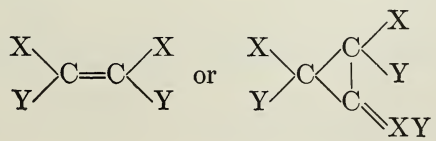
II. On the Unsaturated Compounds

The unsaturated compounds may, first of all, be divided into three categories, namely: I. Those in which two atoms, which may be the same or different, are bound doubly or triply to each other by two or three affinity units, such as olefines; acetylenes; chlorine, $Cl{\equiv}Cl$; oxygen, $O{=}O$; aldehydes, $\begin{matrix} R \\ H \end{matrix}\!\!>\!C:O$; alkylcyanides, $R{-}C{\equiv}N$; nitric acid, $HON\!<\!\begin{matrix} O \\ O \end{matrix}$; sulphur trioxide, $O{=}S\!<\!\begin{matrix} O \\ O \end{matrix}$, etc. II. Those in which an atom itself is unsaturated—i.e., does not exert its maximum valence capacity, as, for instance, amines, $R_3{\equiv}N$; thioethers, $R_2{=}S$; methylene derivatives, etc. We must assume that the remaining affinity units are latent, or, what is far more probable, especially where two or four affinity units are available, that they mutually polarize each other in a manner entirely similar to unsaturated compounds containing doubly or triply linked atoms.

Finally we have a third class of unsaturated compounds: III. Those containing closed atomic chains, such as trimethylene, $\begin{array}{c} CH_2 \\ / \quad \backslash \\ CH_2 \text{——} CH_2 \end{array}$; propylenoxide, $\begin{array}{c} O \\ / \quad \backslash \\ CH_3CH \text{——} CH_2 \end{array}$, etc., which show apparently a saturated molecular system like the paraffines, and yet react in a manner perfectly analogous to olefines and methylene derivatives.

Fundamentally considered these three classes of unsaturated compounds manifest their chemical activity in the same way; they absorb a great variety of other molecules and thus form combinations, called addition products. How does this union take place? An unsaturated compound with its affinities polarized represents, in reality, a saturated system; it cannot, *per se*, show chemical activity. This is also true of molecular systems in which the atoms are bound to one another by single affinity units. The sole basis of reactivity in either case is the presence of a relatively greater or smaller number of dissociated particles. The reactivity of any unsaturated, as well as of a saturated compound, must, in fact, be directly proportional to the ratio of such active particles present. If that ratio is very small, the substance may be entirely inert; if it is greater, absorption of reagents proceeds with regularly increasing speed.

Experience has shown, furthermore, that many unsaturated compounds cannot be isolated, but polymerize spontaneously. It is clear that when the percentage of active particles present in an unsaturated compound becomes relatively great the possibility of their uniting with each other to form condensed molecules increases—in fact, we may imagine a condition in which the active molecules simply cannot be prevented from combining with each other. This shows us why we cannot isolate and keep substances like formaldehyde, $H_2C{=}O$, or alkylcyanates, $ROC{\equiv}N$, in the monomolecular form. Similarly in many cases where attempts were made to isolate methylene derivatives, like mono- and di-phenylmethylene, benzoyl, and acetylmethylene, and cyanmethylenecarboxylate, $\begin{array}{c} CN \\ COOR \end{array}\!\!>C$, a spontaneous polymerization to the di- or tri-molecular systems,

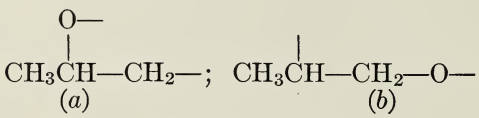


$$\begin{array}{c} X \\ Y \end{array}\!\!>C{=}C<\!\!\begin{array}{c} X \\ Y \end{array} \quad \text{or} \quad \begin{array}{c} X \\ Y \end{array}\!\!>C<\!\!\begin{array}{c} C<\!\!\begin{array}{c} X \\ Y \end{array} \\ | \\ C{=}XY \end{array}$$

took place. One further point with reference to unsaturated compounds must now be presented.

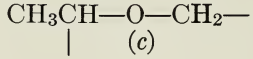
"Intramolecular Rearrangement Shown by Unsaturated Systems":

From the discussion presented above it is obvious that trimethylene and propylenoxide, belonging to class III, must contain a small percentage of active particles; the dissociation of the triatomic ring in the former case can lead to only one form of active molecule—namely, $—CH_2—CH_2—CH_2—$; whereas propylenoxide may give the following three active molecules:



(a) (b)

and



(c)

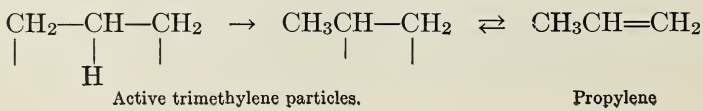
Since propylenoxide absorbs dry ammonia or hydrogen chloride, as was proved by especially careful and exhaustive experiments, giving addition products of the general formula:

$$CH_3CHOH—CH_2X(X{=}Cl \text{ or } NH_2)$$

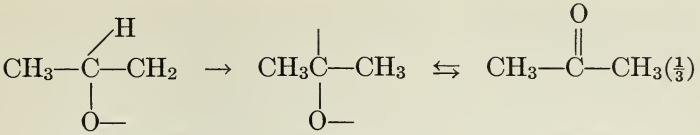
the only possible conclusion that can be reached is that propylenoxide contains relatively more active (*a*) than active (*b*) or (*c*) molecules; consequently the absorption reactions proceed by preference in only one of three theoretically possible directions.

When trimethylene or propylenoxide is heated or placed in contact with various catalytic agents, the percentage of active particles must naturally increase and when a definite limit has been reached a spontaneous transformation of trimethylene into propylene and of propylenoxide into propionaldehyde ($\frac{2}{3}$) and acetone ($\frac{1}{3}$) takes place; both reactions are non-reversible.

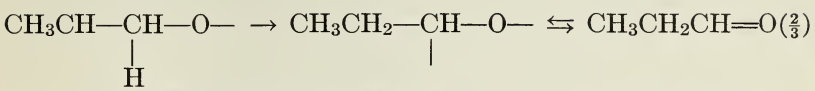
These results can be explained only in the following manner: aside from the increase in active particles, dissociation in other parts of the molecule and especially of hydrogen from carbon must also take place. Consequently the following intramolecular addition reactions finally occur spontaneously:



Active trimethylene particles. Propylene



Active propylenoxide, particles (*a*) Acetone

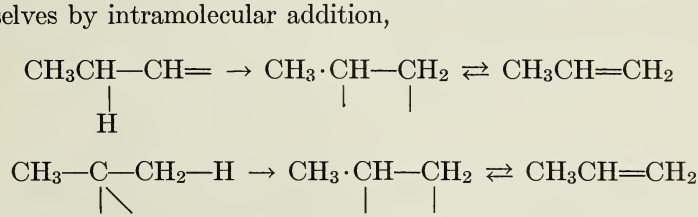


Active propylenoxide, particles (*b*) Propionaldehyde

It is interesting to note that the active (*b*) propylenoxide molecules which are present in smaller ratio suffer rearrangement more readily than the active (*a*) molecules. The active (*c*) molecules, on the other hand, must be present in far smaller amount and certainly no transformation of propylenoxide to vinylmethyloxide, $CH_2{=}CH{-}OCH_3$, takes place.

It is important to realize that propylenoxide, acetone, and propionaldehyde are isomers, but do not stand in a tautomeric relation to one another. This is also true of trimethylene and propylene, as well as of α- and β-amylene and isoamylene, etc.

Similarly it can be rigidly shown by experiment that α- and β-propylidene, $CH_3CH_2CH{=}$ and $(CH_2)_2C{=}$, which are spontaneously combustible substances not capable of isolation as such, transform themselves by intramolecular addition,



into propylene (non-reversible).

There is not the slightest doubt that such intramolecular addition reactions are the basis of the majority of our synthetic methods for making cyclic compounds. The cycloparaffines in Russian petroleum are probably formed from ordinary paraffines by dissociation into hydrogen and methylene derivatives and the latter then spontaneously transform themselves, by intramolecular addition, into penta- and hexa-methylene rings.

"On the Reactions of Paraffines and Benzene Derivatives":

The reactions of paraffines and benzene derivatives towards halogens, nitric and sulphuric acids, whereby substitution products are formed are still interpreted in the text-books from the standpoint of

metalepsis or substitution, although a vast amount of evidence has accumulated which makes this axiomatic assumption improbable.

The fact that ethane and benzene, for instance, decompose into hydrogen and into ethylene and diphenyl at 800° and 600°, respectively, proves that an extremely small percentage of these molecules must exist at ordinary temperatures in an active or dissociated condition,

$$CH_3CH_3 \rightleftarrows CH_3CH_2— + H—$$

and

$$CH_3CH_3 \rightleftarrows C_2H_4 + 2H— \quad \text{or} \quad C_6H_6 \rightleftarrows C_6H_5— + H—$$

The same is true of ammonia,

$$H_3N \rightleftarrows —NH_2 + H— \quad \text{and} \quad 2H— + =NH \quad \text{and} \quad \equiv N + 3H—$$

and of a great variety of other non-ionizable hydrogen compounds. Consequently, when chlorine or nitric acid reacts with benzene or ethane to give the monochlor or mononitro substitution products we have these reagents in the *active molecular* condition, simply uniting by addition with the ethane or benzene particles,

$$\begin{matrix} Cl{=}Cl \\ | \quad | \end{matrix} + H—C_2H_5 \rightarrow \begin{matrix} Cl{=}Cl \\ | \quad | \\ H \quad C_2H_5 \end{matrix}$$

or

$$HO—\overset{\displaystyle O}{\overset{\|}{N}}—O + H—C_6H_5 \rightarrow HO—\overset{\displaystyle O}{\overset{\|}{N}}—OH$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C_6H_5$$

the resulting addition products then lose hydrogen chloride and water, respectively, and thus give the monochlor or nitro substitution product of the mother substance. From this point of view all so-called substitution reactions belong to the category of addition reactions.

What is now especially needed in order to place the reactions of organic chemistry on an exact mathematical basis is a precise method of determining the ratio of active particles present at various temperatures in the case of the unsaturated, as well as the saturated compounds.

As the substances under discussion are almost exclusively non-electrolytes, the sole methods that suggest themselves for this purpose are determinations of the speed of decomposition, as well as of addition reactions.

The above discussion makes it evident that all unsaturated compounds belonging to classes I and III contain a small and relatively

varying percentage of active particles with one or more carbon atoms temporarily in an active or trivalent condition; the same is true of compounds containing hydrogen bound to carbon—paraffines, C_nH_{2n+1}—H, benzene derivatives, etc. The isolation of compounds containing trivalent carbon as such, I believe, however, to be an impossibility. Gomberg's triphenylmethyl, for instance, has recently been proved by him to be a bimolecular aggregate, $C_{38}H_{30}$—not identical with hexaphenylethane—which, however, like the above-mentioned compounds, contains a very small percentage of active triphenylmethyl, $(C_6H_5)_3{\equiv}C$—, particles in dynamic equilibrium with the bimolecular aggregate; as soon as the percentage of triphenylmethyl particles is increased by heat or by means of catalytic agents a spontaneous polymerization to the real hexaphenylethane (non-reversible) takes place.

We are now in a position to consider the evidence showing that methylene and its homologues play a great rôle in many of the fundamental reactions of organic chemistry which have hitherto been explained on the basis of substitution.

III. On the Reactions of the Monatomic Alcohols and the Alkylhaloids

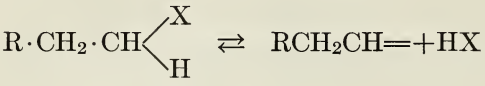
The experiments which first suggest themselves as a means of isolating methylene and its homologues are: I. dissociation of olefines as ethylene:

$$CH_2{=}CH_2 \rightleftarrows 2CH_2$$

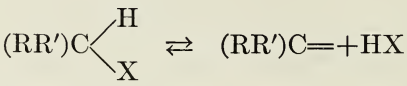
$$CH_3CH{=}CH{-}CH_3 \rightleftarrows 2CH_3CH{=}, \text{ etc.}$$

Since ethylene gives hydrogen and acetylene by heat and the higher olefines also decompose with evolution of hydrogen, there was little prospect of success by experiments in this direction. 2. dehydration of the mono-atomic alcohols, $C_nH_{2n+1}OH$, or removal of halogen hydride from the alkylhalides, $C_nH_{2n+1}X$; naturally only primary and secondary derivatives, RCH_2X and $\begin{matrix} R \\ R \end{matrix}\!\!>\!CHX$(X=OH, Cl, Br, or I), and not tertiary compounds, $R_3{\equiv}C{-}X$, can yield methylene and its homologues. Furthermore, since many of the alcohols and alkylhalides containing more than one carbon atom in the molecule are known to give olefines by dissociation, dehydration, or treatment with alcoholic potash, respectively, the conclusion might naturally at first be drawn that only

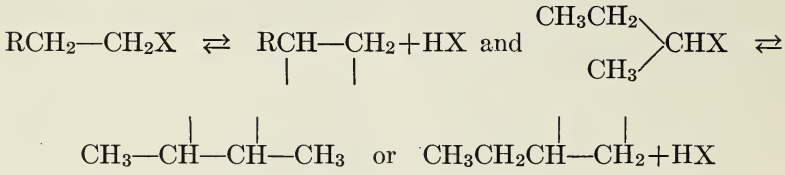
a direct olefine dissociation existed in these cases. From a purely theoretical standpoint, however, it is clear that a primary or secondary alkylhalide or a corresponding alcohol with more than one carbon or hydrogen atom in the molecule may dissociate with loss of halogen hydride or water in two possible ways: it may undergo (1) methylene dissociation, as



and



or (2) olefine dissociation, as

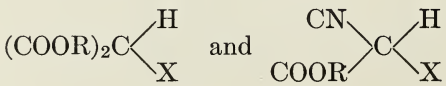


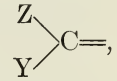
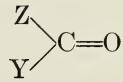
or both kinds of dissociation may take place simultaneously.

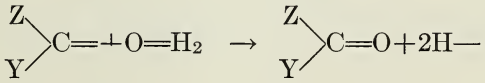
A third kind of dissociation where the hydrogen atom does not come from the atom containing the X or from a carbon atom adjacent to it is also possible and at times important, but it need not be considered in this connection.

An exhaustive study of the primary and secondary alcohols and alkylhalides, covering a period of nine years, has proved very conclusively that these substances undergo methylene dissociation only.

Preliminary experiments with alcohols and alkylhalides where no olefine dissociation is possible, i.e., in the methane, , toluene, , diphenylmethane, , acetone and acetophenone, , , and malonic and cyanacetic ester series

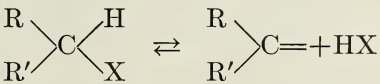


have proved that all these compounds have very low dissociation points—never above 300° in the aromatic nor, with few exceptions, in the aliphatic series. Nevertheless it was found impossible to isolate the methylene derivative as such in any case; there was either a spontaneous conversion to a di- or trimolecular polymer, an olefine or a trimethylene derivative, or a conversion to resinous polymers analogous to azulmic acid and the alkylisocyanide resins. Most important was the discovery that these nascent or active methylene residues  , are always spontaneously combustible, burning often with marvelous evolution of heat to the corresponding oxides,  ; this was not surprising in view of the properties of the methylene derivatives described above. Furthermore, the affinity of unsaturated carbon for oxygen is strikingly shown by the fact that these residues have the power of decomposing water,



with evolution of hydrogen.

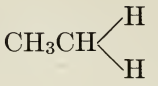
A subsequent investigation of the primary and secondary alcohols and alkylhalides containing more than one carbon atom proved, first of all, that all these substances have comparatively low points of dissociation. In no case was the decomposition point found to be higher than 700°; it was often as low as 160° to 300°. The products of dissociation are water or halogen hydride and C_nH_{2n}, respectively; and the latter, as emphasized above, is invariably methylene or a homologue and never an olefine. This naturally means that all these compounds are partially dissociated in this way at ordinary temperatures, and

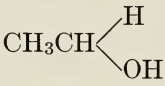


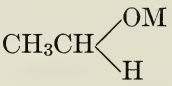
relatively the more the lower the actual decomposition point.

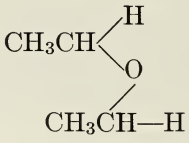
It is, therefore, possible that in all the interactions of the primary and secondary alkylhalides with other substances, such as salts, ammonia, metals, benzene, etc., they do not act as such, but by virtue of being partially dissociated. An enormous amount of evidence has accumulated in favor of this conclusion. Let us consider chiefly the results obtained in the ethyl series, including ethyl alcohol and its

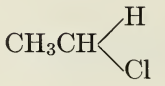
derivatives. The dissociation or decomposition point of the following compounds containing ethyl has been determined with a fair degree of accuracy:

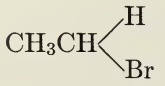
Ethane,  800°

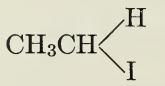
Ethyl alcohol,  650°

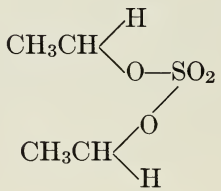
Sodium and potassium ethylate,  250°

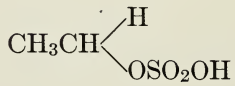
Ethyl ether,  550°

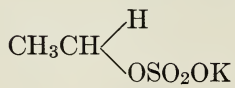
Ethyl chloride,  600°

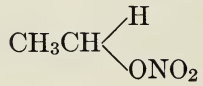
Ethyl bromide,  500°

Ethyl iodide,  400°

Diethyl sulphate,  200°

Monoethyl sulphate,  160°

Ethyl potassium sulphate,  250°

Ethyl nitrate,  200° (?)

Ethane, ethyl chloride, and bromide, when heated to the temperatures named, give ethylene and hydrogen and halogen hydride, respectively, and on cooling these products do not again recombine. We can, therefore, obtain ethylene quantitatively from chloride or bromide of ethyl by simply passing their vapors through tubes heated to the decomposition point. Nevertheless it is impossible to obtain more than very small amounts of ethylene from the ethylhalides by means of alcoholic potash, caustic potash, or quicklime; in these cases ethyl halide is passed over quicklime in tubes to from 300° to 500°. Furthermore, the percentage of ethylene obtained varies remarkably with the temperature, the concentration, and with the nature of the halogen in the alkylhalide used.

The conclusions finally reached from these data and also from an exhaustive study of the behavior of the various alkylhalides, nitrates, sulphates, alkylpotassium sulphates towards heat, sodium ethylate, caustic potash, quicklime, and other salts are that ethylene cannot possibly be a primary product of dissociation of the ethylhalides, sulphates, and nitrates, and of free ethyl alcohol.

The ethylene, when obtained, is formed from ethylidene by an intramolecular addition reaction,

$$\begin{array}{l} \mathrm{H} \\ | \\ \mathrm{CH_2{-}CH{=}} \end{array} \rightarrow \begin{array}{cc} | & | \\ \mathrm{CH_2{-}} & \mathrm{{-}CH_2} \end{array} \rightleftarrows \mathrm{CH_2{=}CH_2}$$

which is not reversible. A similar intramolecular change always, in fact, takes place whenever an olefine is formed, whether from a primary or secondary alcohol, or from a corresponding alkyl halide sulphate or nitrate. This transformation is perfectly analogous to the conversion, discussed above, of trimethylene and of propylenoxide into propylene, propionaldehyde, and acetone.

When ethyl alcohol or ethyl ether is heated to its dissociation point the ethylidene interacts at once in great part with the other dissociation product, water, to give hydrogen and acetaldehyde,

$$\mathrm{CH_3CH{=}} + \mathrm{O{=}H_2} \rightarrow \mathrm{CH_3CH : O + 2H{-}}$$

In the case of ether, since there are two ethylidene molecules to one of water, the atomic hydrogen is, in part, absorbed by ethylidene to give ethane. Finally, a portion of ethylidene, 20 and 37 per cent, respectively, is transformed, by intramolecular addition, into ethylene. The most striking proof that ether is dissociated into water and $2C_2H_4$ particles is the following: on passing ether vapor over phosphorus

pentoxide at temperatures varying from 200° to 400° ethylene is formed quantitatively.

The primary and secondary alcohols and their corresponding ethers being in a state of very slight dissociation at ordinary temperatures, we are able to understand perfectly their behavior towards oxidizing agents. The alkylidenes are all spontaneously combustible substances possessing a great affinity for oxygen. Absolutely pure dry ethyl ether, dissociation point 550°, contains a sufficient percentage of ethylidene particles at ordinary temperatures to burn very slowly in dry oxygen; sodium ethylate, dissociation point 250°, on the other hand, being dissociated to a far greater extent, burns with great violence in dry air. Ethyl alcohol, dissociation point 650°, is not capable of burning in the air; if, however, we increase the percentage of ethylidene particles by means of catalytic agents, enzymes, platinum sponge, etc., it, too, oxidizes readily, with incandescence with platinum sponge, giving acetic acid.

The aldehydes, RCH : O, as has long been known, reduce Fehling's solution and silver solutions with great ease. This is due to the presence of oxyalkylidene particles, $\begin{matrix} R \\ HO \end{matrix}\!\!>\!C=$, which burn at the expense of the oxygen in the water.

The discovery that all primary and secondary alcohols reduce silver oxide to metallic silver in aqueous solution in the presence of caustic alkalies has only very recently been made. The function of the alkali is obviously to form first the metallic alcoholate,

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!C\!<\!\begin{matrix} H \\ OH \end{matrix} + MOH \rightleftarrows \begin{matrix} R \\ R \end{matrix}\!\!>\!C\!<\!\begin{matrix} H \\ OM \end{matrix} + H_2O$$

which, having a far lower dissociation point than the free alcohol, causes a great increase in the percentage of alkylidene particles present; consequently, the following reaction can take place:

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!C=+2H—OH+Ag_2O \rightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!C=(OH)_2+Ag_2+H_2O, \text{ etc.},$$

giving, as the end result, a fatty acid in the case of primary alcohols.

The most striking proof that ethyl alcohol is dissociated only into ethylidene and water,

$$CH_3CH\!<\!\begin{matrix} H \\ OH \end{matrix} \rightleftarrows CH_3CH=+H_2O$$

i.e., contains no ethylene particles, is the following: ethyl alcohol, containing one molecule of aqueous sodium hydroxide, gives, in the cold, with potassium permanganate solution, practically acetic acid only. If any active ethylene particles were present,

$$CH_3CH_2OH \rightleftarrows \begin{matrix} | & | \\ CH_2 & CH_2 \end{matrix} + H_2O$$

these must necessarily, in view of the work of Wagner with olefines and permanganate, be first converted by oxidation to ethylene glycol,

$$3\begin{matrix} CH_2 & CH_2 \\ | & | \end{matrix} + 6H{-}OH + 2KMnO_4 \rightarrow 3\begin{matrix} CH_2 & CH_2 \\ | & | \\ OH & OH \end{matrix} + 2MnO_2 + 2KOH + 2H_2O$$

Analogous results would naturally be expected in the case of all the homologous primary and secondary alcohols. Now a primary alcohol invariably first gives, by oxidation with potassium permanganate or other oxidizing agents, the corresponding fatty acid. Glycols or their oxidation products have never been observed in such cases.

The fact that ethyl alcohol gives glyoxal, glyoxylic, and oxalic acids with nitric acid is no exception to this rule, because these substances result from the hydrolysis and oxidation of isonitrosoacetaldehyde, which is formed by the action of nitrous acid on acetaldehyde as follows:

$$H{-}CH_2CHO + \begin{matrix} O & NOH \\ | & | \end{matrix} \rightarrow HO{-}\underset{\displaystyle CH_2\cdot CH : O}{N}{-}OH \rightarrow \begin{matrix} HON \\ \| \\ CH{-}CH : O \end{matrix} + H_2O$$

The behavior of aldehydes and of primary alcohols towards aqueous or solid caustic potash also leads to the conclusion that only alkylidene dissociation occurs. Ethyl alcohol gives, at 250°, with an excess of caustic potash, hydrogen and potassium acetate quantitatively:

$$CH_3CH\begin{matrix} H \\ \diagup \\ \diagdown \\ OK \end{matrix} + 2KO{-}H \rightarrow CH_3CH{=}+3KO{-}H \rightarrow$$

$$CH_3CH(OK)_2 + 2H + KOH \rightarrow \begin{matrix} CH_3 \\ \diagdown \\ KO \end{matrix}\!\!\diagup C{=}+2H{-}OK + H_2 \rightarrow$$

$$\begin{matrix} CH_3 \\ \diagdown \\ KO \end{matrix}\!\!\diagup C(OK)_2 + 2H + H_2 \rightarrow CH_3C(OK)_2 + 2H_2$$

If any of the potassium ethylate, which is first formed, were dissociated into ethylene and caustic potash,

$$CH_3CH_2OK \rightleftarrows CH_2{=}CH_2 + HOK$$

the olefine must naturally give, besides hydrogen, ethyleneglygol,

$$\begin{array}{l} CH_2{-}CH_2 + 2H{-}OK \\ | \qquad\quad | \end{array} \rightarrow \begin{array}{l} CH_2{-}CH_2 + H_2 \\ | \qquad\quad | \\ OK \quad\; OK \end{array}$$

or its decomposition products; these are, however, not formed. The reaction with potash-lime and primary alcohols is so delicate and accurate that it has been suggested by Hell as a means of determining the molecular weight of an unknown primary alcohol.

As mentioned above, ethyl ether is the chief product when ethyl halides are treated with alcoholic potash or with dry sodium ethylate; this is also true when dry silver oxide and ethyl-halides are used.

These reactions, which have been interpreted by Williamson and others on the basis of double decomposition or of minute ionization, must obviously be attributed to the absorption by the ethylidene of alcohol or of water, which is set free by the action of the halogen hydride particles on the sodium ethylate or silver oxide, respectively,

$$CH_3CH{=}{+}H{-}OC_2H_5 \rightarrow CH_3CH_2OC_2H_5$$

or

$$2CH_3CH{=}{+}H_2{=}O \rightarrow \begin{array}{l} CH_3CH\langle^{H} \\ \qquad\qquad\quad O \\ CH_3CH\langle_{H} \end{array}$$

We are now able to consider an entirely new explanation of the function of sulphuric acid, or of phenyl sulphonic acid, in converting ethyl alcohol into ether. Sulphuric acid acts, first of all, with alcohol at ordinary temperatures to give both mono- and diethyl sulphate; the first stage in the reaction cannot be ascribed to the union of ethylidene, formed by dissociation of alcohol, with free sulphuric acid since ethyl ether, which is relatively more dissociated than alcohol, reacts only very slowly with concentrated sulphuric acid at ordinary temperatures to give monoethyl sulphate. Furthermore, since sulphuric acid itself is completely dissociated into its components sulphur trioxide and water at 400°, it is extremely probable that monoethyl sulphate is

formed by the union of ethylalcohol and sulphur trioxide formed by dissociation as is expressed below:

I. $$H_2SO_4 \rightleftarrows SO_3 + H_2O$$

II. $$\begin{array}{l} O_2S{-}O + H{-}OC_2H_5 \\ \;\;| \quad\;\; | \end{array} \rightarrow O_2S\begin{cases} OH \\ OC_2H_5 \end{cases}$$

Now it is well known that ether formation in a mixture of sulphuric acid and alcohol begins perceptibly only at 95° and proceeds very slowly at that temperature. The favorable temperature for ether manufacture is 140°. This is self-evident in view of the following considerations: primary and secondary ethyl sulphate possess the dissociation points of 160° and 200°, respectively; consequently, these substances must be dissociated to a very great extent into sulphuric acid and one or two molecules of ethylidene, respectively. Addition of alcohol at 140°, therefore, simply necessitates a combination with the ethylidene particles,

$$CH_3CH{=} + H{-}OC_2H_5 \rightarrow CH_3CH_2OC_2H_5$$

to give ether, and this process can naturally go on indefinitely.

When ethyl alcohol is mixed with an excess of concentrated sulphuric acid and heated to 160° no ether, but some ethylene, is formed; in fact, this method is still suggested and used as the best means of preparing ethylene.

The yield of olefine, however, can never be raised above 20 per cent of the theory and the operation is extremely tedious because carbonization and formation of sulphur dioxide takes place to a very marked extent. These results are now easily understood. The ethylidene molecules, formed by dissociation of ethylated sulphuric acid, burn chiefly at the expense of the oxygen present in sulphuric acid,

$$CH_3CH{=} + O{=}SO_2 \rightarrow CH_3CH : O + SO_2$$

and the resulting acetaldehyde is then at once charred by the vitriol present. Only 20 per cent, at the utmost, of the ethylidene particles escape this oxidation by intramolecular conversion to ethylene.

Finally we may summarize the conclusions reached in the above discussion as follows:

The valence of carbon is not a constant. At definite temperatures, which vary remarkably with the nature of the groups bound to it, a carbon atom becomes spontaneously dyad. Below these limits there is dynamic equilibrium between bivalent and quadrivalent carbon. The existence of carbon compounds containing bivalent carbon has been

definitely established; methylene chemistry plays a great rôle in many of the fundamental reactions of organic chemistry.

The conception of substitution or metalepsis, which has been our guide in interpreting the reactions of carbon chemistry since 1833, is no longer tenable. It must be replaced by the conception of dissociation in its broadest sense. Fundamentally speaking, there are but two classes of carbon compounds—the saturated and the unsaturated. Excluding reactions called ionic, a chemical reaction between two substances always first takes place by their union to form an addition product. The one molecule being unsaturated and partially in an active molecular condition absorbs the second molecule because it is partially split or dissociated into two active portions. The resulting addition product then often dissociates spontaneously, giving two new molecules. The similarity of such reactions to those called ionic is at once apparent, but their relationship cannot, in the present state of our knowledge, be clearly understood.

CHAPTER XV

CONCEPTIONS IN REGARD TO THE INDEPENDENT EXISTENCE OF FREE ORGANIC RADICALS

Nef's theoretical conceptions are based upon the assumption of the changing valency of carbon with sharp emphasis upon the importance of considering addition processes in all reactions in organic chemistry. These conceptions were by no means original since von Baeyer in 1894 had explicitly stated that "carbon is *as a rule* tetravalent" and had even suggested that the properties of cyanogen compounds might be explained by assuming the presence of bivalent carbon. The significance of addition processes in organic reactions had also been pointed out by the American investigator, Arthur Michael. Nef's contribution consisted in extending the scope of these conceptions and in establishing them more firmly on the basis of experimental evidence. By supplying the additional assumption of molecular dissociation he was able to combine several sets of more or less isolated ideas into a theoretical system which was capable of including a variety of chemical processes and which was also plastic enough to lend itself to the interpretation of new reactions.

In summing up Nef's particular achievements it may be said that he was able to demonstrate the presence of bivalent carbon in several groups of organic compounds, among which may be mentioned the alkyl- and aryl-isocyanides, RN=C, and the mono- and di-substituted acetylenes. The reactions of these and other similar classes of substances were interpreted by assuming that the relative reactivity of a given compound depends primarily upon dissociation phenomena. All of the reactions of methane, for example, are supposed to be preceded by a preliminary dissociation of the substance in either of two ways:

I. $CH_4 \rightleftarrows CH_3+H$

II. $CH_4 \rightleftarrows CH_2+2H$

Dissociation is supposed to take place even at ordinary temperatures and the fact that it has been impossible as yet to isolate free methylene is explained by assuming that free radicals instantly polymerize. It

may be mentioned in this connection that recent experiments which have aimed to prepare free diarylmethylene by splitting off nitrogen from aryl substituted aliphatic diazo compounds have not achieved the desired result.[1]

Nef undoubtedly revived a belief in the possibility of the independent existence of organic radicals. It may be remembered that this possibility had engaged the attention of chemists for many years but that attempts to isolate free radicals had ultimately been abandoned. While Nef did not himself succeed in actually demonstrating the existence of such a substance, this accomplishment may nevertheless be accredited to a member of his school.

In 1900 M. Gomberg[2] discovered triphenylmethyl as the result of an investigation which was undertaken with a view to establish definitely the constitution of tetraphenylmethane. Since the problem involved the preparation of hexaphenylethane, $(C_6H_5)_6C_2$, and since the Fittig synthesis and other of the usual methods had failed to give this hydrocarbon, Gomberg tried to prepare it by treating triphenyl chlormethane and triphenyl brommethane with finely divided metals such as Hg, Ag, Zn, Cu, etc. Under ordinary conditions the only product of this reaction is a substance which contains oxygen. When however, the experiment was conducted in an atmosphere of carbon dioxide, an orange-colored solution was formed, and this, when evaporated in the absence of oxygen, gave crystals of what appeared to be hexaphenylethane. But although the results of the analysis pointed to this conclusion, the properties of the substance were so remarkable as to leave the matter in some doubt. For example, it forms colorless crystals which gradually change to yellow in the air and which, when dissolved in a number of different solvents, give yellow solutions. But above all it is chemically so reactive as to appear to be strongly unsaturated. Such a condition of seeming unsaturation was explained by Gomberg as due to the presence of trivalent carbon, and the substance was regarded as an example of a triaryl substituted free methyl radical:

$$(C_6H_5)_3C—$$

Many other formulas have been suggested for this very interesting substance as the result of a discussion which immediately arose in regard to its constitution. This discussion has continued up to the present time and will be reviewed more fully later in the chapter on the Relation of Color to Chemical Constitution. At the present time it need only

[1] Staudinger, Ber., **49**, 1923 (1916).

[2] Ber., **33**, 3150 (1900); also Schmidlin, "Das Triphenylmethyl," Stuttgart, 1914.

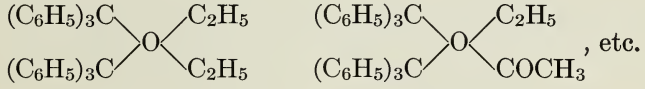
be said that the reactions of this extraordinary substance are most readily understood on the basis of the triphenylmethyl formula of Gomberg. For example, the substance is readily oxidized to a peroxide by the oxygen of the air:

$$2(C_6H_5)_3C—+O_2=(C_6H_5)_3CO\cdot O\cdot C(C_6H_5)_3$$

The product is a colorless compound which crystallizes readily, is only slightly soluble, and possesses the properties of a saturated substance. Triphenylmethyl also reacts readily with halogen, especially iodine, according to the equation:

$$2(C_6H_5)_3C—+I_2=2(C_6H_5)_3CI$$

This product, in the presence of an excess of halogen, reacts to give a perhalide of the formula $(C_6H_5)_3CI\cdot I_5$ and, in the presence of metallic halides such as $AlCl_3$, $SnCl_4$, $SbCl_3$, etc., it reacts to give organometallic compounds having the general character of double salts. Triphenylmethyl also readily adds benzene, ether, esters, etc., to give compounds having the formulas:



, etc.

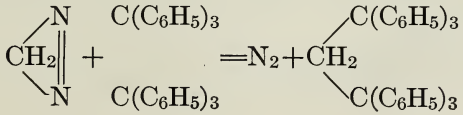
If nitric oxide is mixed with carbon dioxide and conducted into an ethereal solution of triphenylmethyl, a reaction takes place which is accompanied by the momentary appearance of a bluish green color, due to the formation of nitrosotriphenylmethyl. The latter polymerizes immediately to give a binitrosyl compound which is colorless:

$$(C_6H_5)_3C+NO \rightarrow \underset{\text{Bluish Green.}}{(C_6H_5)_3C\cdot NO} \rightarrow \underset{\text{Colorless.}}{(C_6H_5)_3C(NO)_2C(C_6H_5)_3}$$

Nitrogen dioxide under the same conditions gives a mixture of a nitroderivative and an ester of nitrous acid which can be separated:

$$2(C_6H_5)_3C+2NO_2=(C_6H_5)_3C\cdot NO_2+(C_6H_5)_3C\cdot ONO$$

Unsaturated organic radicals add triphenylmethyl in much the same way. For example methylene, which is formed as an intermediate product in the decomposition of diazomethane, reacts to give hexaphenylpropane:



Diphenylnitride likewise reacts to give completely substituted derivatives of methylamine:

$$(C_6H_5)_2N+C(C_6H_5)_3=(C_6H_5)_2N\cdot C(C_6H_5)_3$$

These and a great variety of other reactions which need not be reviewed at this time, serve to demonstrate the preeminently unsaturated properties of the substance. Attempts to confirm the above formula for triphenylmethyl by means of molecular weight determinations were then made.

When the molecular weight of the substance was determined in fused naphthalene by means of the freezing-point method, values of 330 and 370 were obtained. These are both considerably higher than 243, which represents the value calculated on the basis of the simplest molecular formula of the substance. These values are, however, also considerably lower than the molecular weight of hexaphenylethane, which equals 486. In other solvents such as nitrobenzene, dimethyl aniline, *para*-bromtoluene, and phenol, a value averaging 477 was obtained and it must therefore be assumed that hexaphenylethane is present in these solutions. Gomberg explains the cryoscopic behavior of solutions in naphthalene very simply by supposing that hexaphenylethane dissociates in this solvent according to the equation

$$(C_6H_5)_3C\cdot C(C_6H_5)_3 \rightleftarrows 2(C_6H_5)_3C—$$

Since the condition of equilibrium in such a system as this would depend upon temperature, concentration, and the nature of the solvent, it is easy to see why the behavior of the substance should be entirely different when dissolved in other solvents. This explanation, which was later endorsed by Wieland,[1] has been the subject of much discussion, but has finally come to be generally accepted as a result of the researches of Schlenk and Mair, J. Piccard and others.

Schlenk and Mair [2] determined the molecular weight of hexaphenylethane in benzene and calculated from their results that the degree of dissociation into triphenylmethyl is 29.9 per cent. J. Piccard [3] has also succeeded in demonstrating by means of colorimetric observations that a condition of equilibrium exists in solutions of hexaphenylethane. He discovered for example that the product which is obtained as a result of the action of metals upon triphenylmethyl chloride shows a molecular weight which corresponds to hexaphenyl ethane when examined in concentrated solutions but that this value decreases in proportion

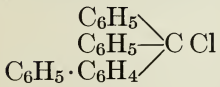
[1] Ber., **42**, 3029 (1909).

[2] Annalen der Chemie, **394**, 179 (1912).

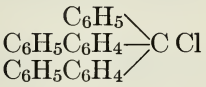
[3] Annalen der Chemie, **381**, 349 (1911); also Ber., **48**, 1097 (1915).

to dilution. This change is accompanied by a marked change in the color of the solution. For example, when a five per cent solution of the substance in ether is diluted with ether which is free from air, in an atmosphere of carbon dioxide, it was observed that the solution, which was originally light yellow, became more and more intensely colored until finally it was changed to a reddish orange. This process is reversible and on evaporation of the solvent the strong color gradually disappears and at the same time the values representing the molecular weight of the dissolved substance gradually increase.

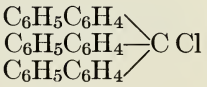
In spite of these discoveries weak points remained in the chain of evidence supporting the assumption of the existence of a free methyl radical, but these were finally strengthened as a result of the researches of Schlenk, who succeeded in preparing other substances with properties similar to those which have been noted in the case of triphenylmethyl. These substances were obtained by treating solutions of



I



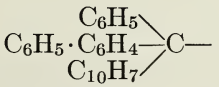
II



III

with active copper and are analogous to triphenylmethyl in every way except that while the latter dissolves to give pale yellow solutions, I gives orange, II gives deep red, and III gives deep violet colorations.

Of these substances the first and second are colorless in solid form, while the third has a violet color and is very unstable. The molecular weights of these respective substances have been determined and results show that the two colorless compounds resemble hexaphenylethane in being bimolecular, while the third is monomolecular and must therefore possess the formula $(C_6H_5 \cdot C_6H_4)_3C—$. This free organic radical when perfectly pure and dry consists of a gray-green crystalline powder which melts at 186° and is extremely sensitive to oxygen whether in the solid state or in solution. Schlenk,[1] in co-operation with his students, has been able to obtain other free organic radicals, as for example,

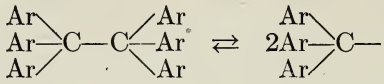


Phenyl-*p*-biphenyl-*a*-naphthyl methyl

and has found that they are all highly unsaturated, exceedingly sensitive to oxygen, and intensely colored. The property of color will be referred to in greater detail in the next chapter.

[1] Annalen der Chemie, **394**, 195 (1912).

It has been noted that substances which correspond to I and II give highly colored solutions. This is explained by supposing that such colored solutions contain equilibrium mixtures of the bi- and mono-molecular modifications:



and that a relatively higher percentage of the latter is present than in the corresponding solutions of hexaphenylethane. It has been observed, for example, that while hexaphenylethane is dissociated to the extent of 10 per cent in a given solvent, the dissociation of I is equal to 15 per cent, that of II is equal to 80 per cent, and III is completely dissociated into the free radical.

The naphthyl group has an even stronger influence upon dissociation than the biphenyl group. Thus for example while tetraphenyldibiphenylethane

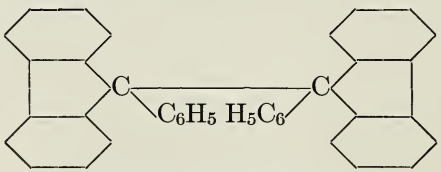
$$\begin{matrix}(C_6H_5)_2 & & (C_6H_5)_2\\ C_6H_5\cdot C_6H_4 & C\text{—}C & C_6H_4\cdot C_6H_5\end{matrix}$$

is dissociated only to the extent of 15 per cent, tetraphenyl dinaphthylethane

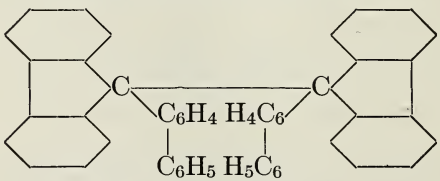
$$\begin{matrix}(C_6H_5)_2 & & (C_6H_5)_2\\ C_{10}H_7 & C\text{—}C & C_{10}H_7\end{matrix}$$

is dissociated under the same conditions to the extent of 60 per cent.

It would seem to follow that derivatives of benzene which possess still denser groupings of the substituents as, for example:



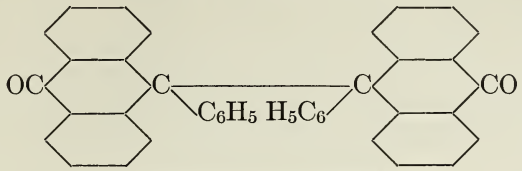
Dibiphenylene-diphenylethane



Dibiphenylene-dibiphenylethane

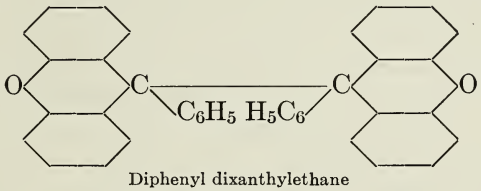
would dissociate even more completely than those which have just been mentioned, but this is not the case. Both substances are undis-

sociated in low boiling solvents and only slightly dissociated at high temperatures. Of the following substances I, II and III:



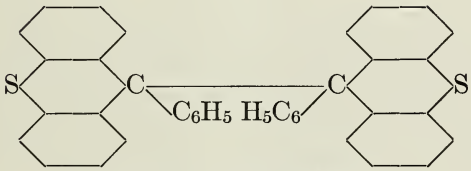
Diphenyl dianthronylethane

I



Diphenyl dixanthylethane

II



Diphenyl dithioxanthylethane

III

the first dissociates to give 33 per cent, the second to give 82 per cent, and the third to give 14 per cent of the free organic radical. It may be added that hexanitroethane

$$(NO_2)_3C—C(NO_2)_3$$

is a colorless fairly stable substance which melts at 142° and which appears to be undissociated in its solutions.

In summing up the present status of this investigation it may be said that the presence of trivalent carbon in the above series of compounds is generally conceded, and that free organic radicals are assumed to exist not only in solution, but in certain instances even in the solid state. The further question as to whether such radicals are ionic in character, as indicated by the equation

$$(C_6H_5)_3COH+HCl \rightarrow (C_6H_5)_3C'+Cl'+H_2O$$

has been answered in the negative by K. H. Meyer and H. Wieland.[1] A systematic study of the absorption spectra of these substances shows

[1] Ber., 44, 2557 (1911).

that triphenylmethyl and all of its triaryl substitution products possess very characteristic band spectra, and that even at great dilutions sharply differentiated bands are plainly visible. Ionized solutions of carbinol salts, on the other hand, all show continuous absorption which shades off much sooner in the region of the short wave lengths. This seems to demonstrate that triphenylmethyl, $(C_6H_5)_3C—$, together with its derivatives, is distinctly different from the triphenylmethyl ion $(C_6H_5)_3C—$.

The mechanism of the formation of triphenylmethyl has been explained by supposing that six such voluminous substituents as phenyl are unable to accommodate themselves within the limits of the ethane molecule. Assuming that the formation of hexaphenylethane is possible, the crowding produced by the presence of such dense groupings might easily give rise to a condition of strain, which in certain cases might lead to the decomposition of the substance and in other cases might even be so great as to prevent its initial formation. If these assumptions are correct it should follow that tetraphenylmethane would have the same properties which have been noted in the case of hexaphenylethane since there is still greater crowding within its molecule. Such a conclusion is, however, not in harmony with the fact that tetraphenylmethane has been observed to be a very stable substance which distills without decomposition under atmospheric pressure and does not resemble hexaphenylethane in any respect. It would, therefore, seem that steric influences do not play the decisive rôle in determining the relative stability of the substances in question.

The most plausible explanation of the phenomena which has been offered up to the present time is that which was advanced by Thiele in 1901 [1] and which supposes that in addition to steric influences, other influences are operative in the form of small residual affinities present on the carbon atoms of the phenyl groups. In triphenylmethyl three sets of such affinities act upon the carbon atom of the methyl group with the result that practically the total affinity of this atom is engaged and little remains with which to hold a fourth atom or group within the molecule. This accounts for the ease with which such a radical dissociates and also for the fact that under certain circumstances the trivalent condition represents the only possible arrangement.[2]

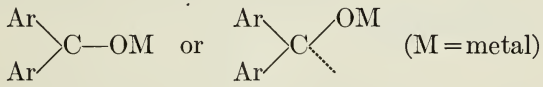
In 1891 E. Beckmann and T. Paul [3] discovered that ketones such as benzophenone, phenyl-α-naphthylketone, and others react with sodium to give intensely colored addition products which consist of

[1] Annalen der Chemie, **319**, 134 (1901).

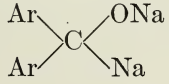
[2] Compare Pummerer and Frankfurter, Ber., **47**, 1472, 2957 (1914).

[3] Annalen der Chemie, **266**, 1 (1891).

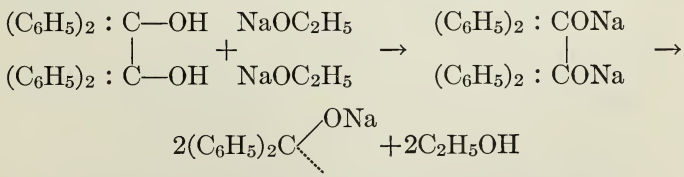
one atom of sodium to one molecule of ketone. Twenty years later W. Schlenk and co-workers [1] repeated this work because they suspected that the phenomenon might be associated with the presence of trivalent carbon. They studied the behavior of the alkali metals, especially K, Na and Li in perfectly dry, air-free solvents, such as ether and benzene, and found that no trace of hydrogen was evolved during the course of the reaction. The resulting compounds belong to a class known as metal-ketyls and resemble the class of triarylmethyls in that they are intensely colored and extremely sensitive to the oxidizing action of the air. That they are monomolecular has been demonstrated in the case of the addition product which is formed by the action of potassium upon phenylbiphenyl ketone, $C_6H_5COC_6H_4 \cdot C_6H_5$.[2] The analogy which exists between such compounds and derivatives of triphenylmethyl is indicated by the formula:



in which the metal is represented as in union with oxygen. It is assumed that the saturation of the groups ONa, OK, etc., requires such a large fraction of the total affinity of the central carbon atom that the fourth valence of this atom is reduced to the value of a residual valence. The presence of free affinity in the molecule is shown by the ease with which the substance adds a second atom of sodium to form reddish colored di-sodium salts of the formula:

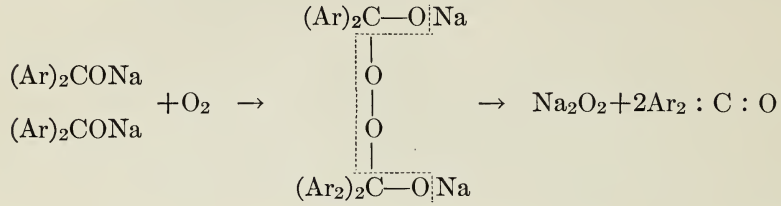


Sodium benzophenone may be prepared in other ways than by the action of this metal upon the ketone. It is formed for example when benzophenone is treated with sodium amalgam or sodium alcoholate in dry ether. Schlenk explains the latter action by supposing that the sodium salt of benzopinacone is formed as a primary product and that this then breaks down to give two free radicals:

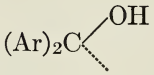


[1] Ber., **44**, 1182 (1911); **46**, 2840 (1913); **47**, 486 (1914).
[2] Ber., **46**, 2840 (1913).

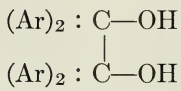
The metal-ketyls resemble the triarylmethyls in being very sensitive to the action of oxygen. It has not as yet been demonstrated, however, that in this case organic peroxides are formed, although it is possible to assume that intermediate products of this character are present in the reaction mixture and that they decompose immediately according to the equation:



The action of water upon sodium benzophenone results primarily in the formation of the radical



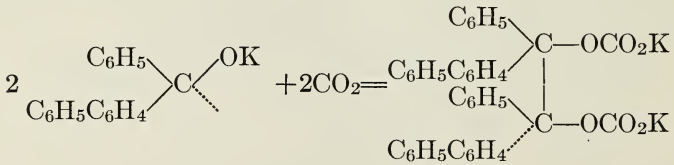
which either polymerizes to give a pinacone



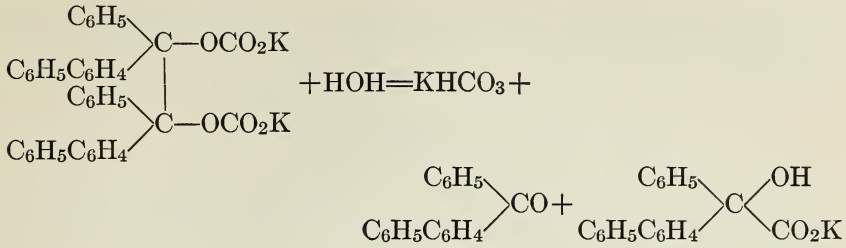
or rearranges to give a mixture of ketone and carbinol:

$$2Ar_2C\cdot OH \rightarrow Ar_2\cdot CO + Ar_2CHOH$$

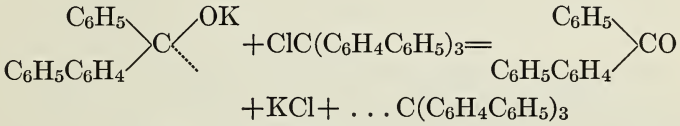
Iodine reacts smoothly with potassium diphenylketone with the result that the free ketone is quantitatively regenerated. The action of carbon dioxide takes place according to the equation



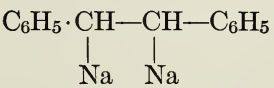
and the resulting compound is decomposed by water to give a mixture consisting of the original ketone, acid potassium carbonate, and phenylbiphenyl glycollic acid:



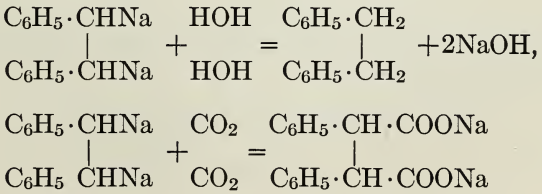
The potassium derivative of phenylbiphenyl ketone also reacts with the corresponding halogen derivative of methane to give tribiphenylmethyl:



The fact that ketones are able to combine not only with one but also with two atoms of sodium led Schlenk to assume that the reaction might possibly belong to the ordinary type of simple addition to unsaturated double bonds and he, therefore, investigated the question from this point of view. As the result of a series of experiments in regard to the behavior of sodium upon compounds which contain unsaturated linkages other than carbonyl, Schlenk made the surprising discovery that under favorable conditions unsaturated compounds with the atomic groupings, C=C, C≡C, C≡N and N=N will add sodium and that this action is accompanied by a decrease in the unsaturated condition of the substance. For example, stilbene reacts to give a violet brown derivative:



which reacts with water to give diphenylethane and sodium hydroxide (*a*) and which adds carbon dioxide to give the sodium salt of diphenylsuccinic acid (*b*)



Oxygen decomposes the sodium derivatives of stilbene according to the equation

$$\begin{array}{l} C_6H_5\cdot CHNa \\ \quad | \\ C_6H_5\ CHNa \end{array} + \begin{array}{c} O \\ \| \\ O \end{array} = \begin{array}{l} C_6H_5{-}CH \\ \quad \| \\ C_6H_5{-}CH \end{array} + Na_2O_2$$

Asymmetrical diphenylethylene also reacts with sodium in ethereal solution but the product in this case is a brick red di-sodium derivative of tetraphenylbutane:

$$2(C_6H_5)_2C{=}CH_2 + 2Na = 2\left(\begin{array}{l}(C_6H_5)_2C\cdot Na \\ \quad | \\ \quad CH_2\ldots\end{array}\right) \rightarrow \begin{array}{l}(C_6H_5)_2C\cdot Na\ Na\cdot C(C_6H_5)_2 \\ \quad | \qquad\qquad\quad | \\ H_2C{-}{-}{-}{-}{-}CH_2\end{array}$$

I II

The carbon atom in diphenylethylene to which the two phenyl groups are attached is much more reactive towards metals than the other ethylene carbon atom and Schlenk therefore assumes that the first atom of sodium adds in this position to give the above unstable intermediate product (I). He also assumes that the rate of reaction with which two such radicals polymerize is greater than that with which a second sodium atom can add so that the final product is as indicated (II). Addition of carbon dioxide takes place readily as in the preceding cases:

$$\begin{array}{l}(C_6H_5)_2C\cdot CH_2CH_2C(C_6H_5)_2 \\ \quad | \qquad\qquad | \\ \quad Na \qquad\quad Na\end{array} + CO_2 \rightarrow \begin{array}{l}(C_6H_5)_2C\cdot CH_2\cdot CH_2\cdot C(C_6H_5)_2 \\ \quad | \qquad\qquad\quad | \\ \quad COONa \qquad COONa\end{array}$$

Benzophenone-phenylimide, $(C_6H_5)_2C{=}N\cdot C_6H_5$, reacts with sodium to give

$$\begin{array}{l}(C_6H_5)_2C{-}NC_6H_5 \\ \quad | \quad | \\ \quad Na\ Na\end{array}$$

and this substance shows the same general properties as others of its class. It reacts with water to give a product in which the two atoms of sodium have been replaced by hydrogen,

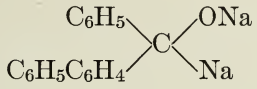
$$(C_6H_5)_2CH\cdot NHC_6H_5$$

and adds carbon dioxide in the usual way to give the sodium salt of the following dicarboxylic acid:

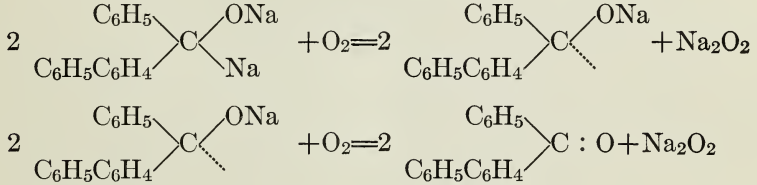
$$\begin{array}{l}(C_6H_5)_2C{-}{-}{-}{-}N{-}C_6H_5 \\ \quad | \quad\quad | \\ \quad CO_2Na\ CO_2Na\end{array}$$

Azobenzene also reacts with metallic potassium to give a product which is analogous in all respects to those which have just been described.

In the case of the di-sodium derivatives of the ketones, as for example



it should be noted that the two sodium atoms are different in their properties, in that the one which is in union with carbon is more reactive than the other. Careful treatment of such a substance with either oxygen or iodine might very easily result in the formation of compounds of the metal-ketyl type, although the latter are so unstable that they would immediately rearrange to give the free ketone and sodium peroxide in the presence of an excess of the reagent:



There are, of course, other interpretations of the action of sodium upon ketones than that which assumes the formation of compounds which contain trivalent carbon. Schmidlin[1] supposes, for example that metal-ketyls are analogous in constitution to the highly colored molecular compounds which are formed by the action of metallic chlorides upon ketones, and this possible solution of the problem will be considered again in some detail in the chapter on Color and Constitution.

The question of the existence of free organic radicals has received further elucidation as a result of the recent investigation of W. Schlenk and his students who have prepared and studied a large number of labile compounds which contain sodium in union with organic radicals. Schlenk and Ochs[2] have, for example, succeeded in separating sodium triphenylmethyl $(C_6H_5)_3CNa$ and have found that it very closely resembles the alkyl magnesium compounds discovered by Grignard, but possesses even greater chemical reactivity. Schlenk and Holtz[3] have prepared the following organo-metallic compounds: sodium methyl, lithium methyl, sodium ethyl, lithium ethyl, sodium propyl, sodium *n*-octyl,

[1] "Das Triphenylmethyl," p. 186, Stuttgart, 1914.
[2] Ber., **49**, 608 (1916).
[3] Ber., **50**, 262 (1917).

sodium phenyl, lithium phenyl and sodium benzyl. With the exception of the latter:

$$NaCH_2C_6H_5$$

which is intensely red, these compounds are all colorless and are either insoluble and amorphous or else soluble in benzene and crystalline. All decompose without melting when heated and are so unstable that they are spontaneously inflammable in the air. The inflammability decreases, however, in proportion as the alkyl radical increases in size. The question as to whether the metal is in the same form of combination in the colored as in the colorless compounds must be left for detailed consideration in the next chapter, and the present discussion will be confined to a review of certain properties of these substances which are of immediate interest.

It is well known that nitrogen does not usually exercise all of its five valencies in attracting similar atoms or groups of atoms. For example, compounds which contain pentavalent nitrogen are stable only when one or even two of the nitrogen valencies are exercised in holding groups which are chemically different from the others, as is the case in $(CH_3)_4NCl$, $(CH_3)_4N\cdot NO_3$,[1] etc., while compounds such as $(CH_3)_5N$ have not as yet been obtained although various attempts have been made to prepare them. Quite recently, however, Schlenk and Holtz [2] have succeeded in synthesizing a substance in which nitrogen appears to be in union with five carbon residues. This has been accomplished by the ingenious device of treating sodium triphenylmethyl with tetramethylammonium chloride:

$$(C_6H_5)_3CNa + Cl\cdot N(CH_3)_4 = NaCl + (C_6H_5)_3C\cdot N(CH_3)_4$$

The reaction, which seems to be one of double decomposition, takes place smoothly and the product consists of glistening red crystals which have a blue metallic luster. A similar substance which consists of a fine red powder is obtained when sodium benzyl is treated with tetramethyl ammonium chloride:[3]

$$C_6H_5\cdot CH_2\cdot Na + ClN(CH_3)_4 = NaCl + C_5H_6\cdot CH_2\cdot N(CH_3)_4$$

Both substances are extremely sensitive to the oxygen of the air and react with water and carbon dioxide according to the equations:

$$(C_6H_5)_3C\cdot N(CH_3)_4 + HOH = (C_6H_5)_3CH + HON(CH_3)_4$$

$$C_6H_5\cdot CH_2\cdot N(CH_3)_4 + HOH = C_6H_5\cdot CH_3 + HON(CH_3)_4$$

$$(C_6H_5)_3C\cdot N(CH_3)_4 + CO_2 = (C_6H_5)_3\cdot C\cdot CO_2\cdot N(CH_3)_4$$

[1] Compare A. Lachman, Ber., **33**, 1035 (1900).

[2] Ber., **49**, 603 (1916).

[3] Ber., **50**, 274 (1917).

It will be noted in the last equation that carbon dioxide enters the molecule and assumes a position between the triphenylmethyl radical and the nitrogen. This is exactly analogous to what takes place in the case of sodium triphenylmethyl, viz.,

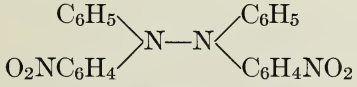
$$(C_6H_5)_3CNa + CO_2 = (C_6H_5)_3CCO_2Na,$$

so that it seems reasonable to conclude that the substituted ammonium radical plays the part of the metal in triarylmethyl tetramethylammonium compounds. Taken as a whole the phenomenon serves to emphasize the truth of a statement which is very frequently made in chemistry, namely that the most important factor in determining the character of a chemical compound is not the nature of the elements which compose it but the arrangements of these elements as shown in the chemical constitution of the molecule.[1]

The chemistry of free organic radicals has recently been supplemented by a study of organic radicals which contain nitrogen. Developments in this field are due in large measure to the researches of H. Wieland who in the course of preparing bi-tertiary aromatic hydrazines discovered that the stability of the union between the two nitrogen atoms is very greatly influenced by the character of the aromatic substituents. For example, colorless tetraphenyl-hydrazine is so unstable that it readily dissociates into radicals which contain bivalent nitrogen and which may be distinguished by the fact that they possess a yellow color.

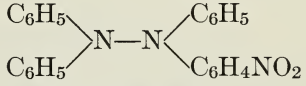
$$(C_6H_5)_2N \cdot N(C_6H_5)_2 \rightarrow 2(C_6H_5)_2N$$

Decompositions of this type may be retarded by the substitution of such groups as C_6H_5 and NO_2 or accelerated by the substitution of CH_3, OCH_3, etc.[2] In the following series of compounds for example the tendency to dissociation increases in passing from the first to the last member:



p-Dinitrotetraphenyl hydrazine

I



p-Mononitrotetraphenyl hydrazine

II

p-Tetrabiphenyl hydrazine

III

Tetraphenyl hydrazine

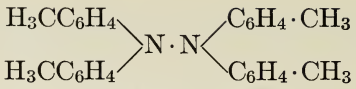
IV

[1] Compare Kehrmann, Ber., **47**, 3055 (1914).

[2] H. Wieland, "Die Hydrazine," p. 72, Stuttgart, 1913; also Ber., **48**, 1078, 1098, 1112 (1915).

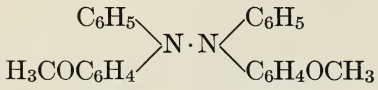
p-Ditolyldiphenyl hydrazine

V



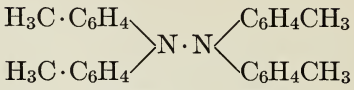
p-Tetratolyl hydrazine

VI



p-Dianisyl diphenylhydrazine

VII

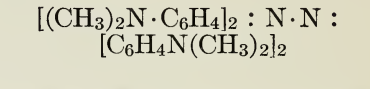


p-Tetratolyl hydrazine

VIII

p-Tetraanisyl hydrazine

IX



Tetra- [*p*-dimethylaminophenyl] hydrazine

X

Since the hydrazines are colorless while the bivalent radicals into which they dissociate are yellow the change may be followed colorimetrically. The first two members show no trace of dissociation but succeeding members give evidence of an ever-increasing dissociation, if comparisons are made at 90°. Since the radicals which form in this way polymerize readily and since, therefore, the phenomenon of color is only transitory, dissociation may be detected more readily by subjecting the solid hydrazine to the action of cathode rays. Tetraphenyl-hydrazine, for example, becomes intensely green under the influence of cathode rays but loses this color at once when the emanation is withdrawn.[1] Solutions of the last three hydrazines, on the other hand, may be studied spectroscopically since it has been observed that even at low temperatures these three solutions contain considerable amounts of the free radicals. J. Piccard[2] has, for example, investigated the absorption spectra of tetraanisyl-hydrazine in solutions of different concentrations and demonstrated the presence of a free nitrogen radical which is green in color. Molecular weight determinations, on the other hand, have been used to follow the dissociation of tetra-[*p*-dimethylaminophenyl]-hydrazine and it has been demonstrated with certainty that it is dissociated into its free radical to the extent of 10 per cent in benzene and of 21 per cent in nitrobenzene solution.[3]

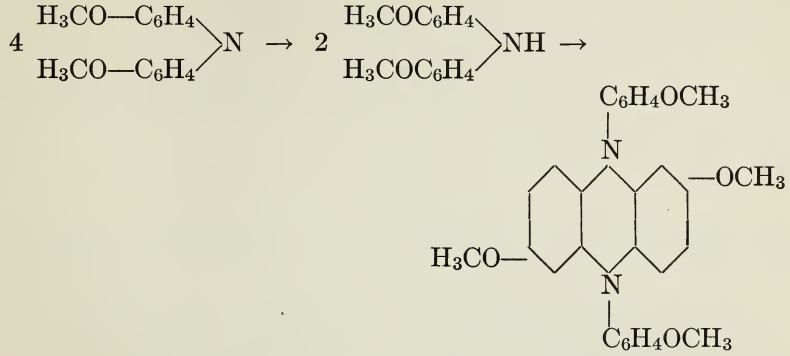
Free diaryl-nitrogen radicals may be said to resemble the inorganic radical NO, although they are much less stable. They are less capable

[1] Hexaphenylethane behaves in the same way.

[2] Annalen der Chemie, **381**, 347 (1911); also Wieland, "Die Hydrazine," pp. 75 and 76.

[3] Ber., **48**, 1078 (1915).

of maintaining an independent existence than triphenylmethyl, since even in solution they are extremely sensitive to changes in temperature and rearrange spontaneously to give a mixture of a reduction and a polymerization product (perazine):



In boiling benzene this transformation requires from ten to thirty minutes.

Nitric oxide is the characteristic reagent which is used to detect the presence of radicals of the diaryl-nitrogen type just as oxygen is a characteristic reagent for detecting triarylmethyl radicals. Addition takes place smoothly according to the equation:

$$Ar_2N + NO = Ar_2N \cdot NO$$

and, in the case of tetraanisyl-hydrazine and tetra-(*p*-dimethylaminophenyl)-hydrazine, proceeds rapidly even at ordinary temperatures. In the case of those hydrazines which dissociate only upon heating a temperature of from 80° to 100° is necessary for the reaction.

Addition reactions between diaryl-nitrogen radicals and triarylmethyl have been observed

$$Ar_2N + C(C_6H_5)_3 = Ar_2N \cdot C(C_6H_5)_3$$

and the resulting compounds have been found to be relatively very stable, showing no tendency to decompose below temperatures of 130–140°.

According to the investigations of Wieland and Reverdy [1] and Wieland and Offenbächer radicals also exist which contain univalent and tetravalent nitrogen. Wieland with M. Offenbächer [2] and K. Roth [3] has recently succeeded in obtaining diaryl derivatives of nitrogen peroxide by processes which involve the elimination of hydrogen from diphenyl

[1] Ber., **48**, 1112 (1915).
[2] Ber., **47**, 2111 (1914).
[3] Ber., **53**, 210 (1920).

hydroxylamine and also from certain of its derivatives in which the hydrogen of the benzene ring has been substituted:

$$(C_6H_5)_2NOH-(H) \rightarrow (C_6H_5)_2N{=}O$$

Diphenyl nitrogen oxide itself is a substance which crystallizes well and which resembles NO_2 in possessing a deep red color and a similar characteristic band absorption. Like nitrogen peroxide this substance behaves as if it were a free radical. For example, it combines readily with nitrogen peroxide:

$$(C_6H_5)_2NO+NO_2 \rightarrow (C_6H_5)_2\overset{\overset{O}{\|}}{N}\cdot NO_2 \rightarrow (O_2NC_6H_4)(C_6H_4)NOH$$

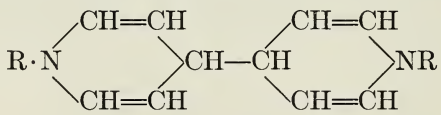
$$\rightarrow (NO_2C_6H_4)(C_6H_5)N{=}O \rightarrow (O_2NC_6H_4)(C_6H_5)\overset{\overset{O}{\|}}{N}\cdot NO_2$$

$$\rightarrow (O_2NC_6H_4)_2NOH \rightarrow (O_2NC_6H_4)_2N{=}O$$

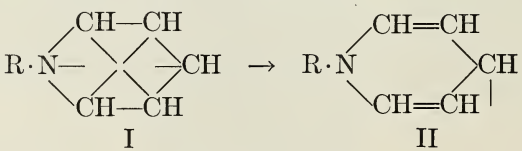
The product which is obtained in this way is capable of reacting with certain other similar unsaturated substances such as triphenylmethyl to give corresponding addition products:

$$(O_2NC_6H_4)_2N{=}O+C(C_6H_5)_3 \rightarrow (O_2NC_6H_4)_2\overset{\overset{O}{\|}}{N}\cdot C(C_6H_5)_3$$

Another radical containing tetravalent nitrogen is supposed to be formed as an intermediate product when quaternary alkyl derivatives of pyridine are treated with sodium amalgam. The final product of this reaction is N,N′-dialkyl-γ, γ'-tetrahydro-γ, γ'-dipyridyl:



The same substance is formed as a result of the electrolysis of quaternary alkyl pyridine salts. According to Bruno Emmert [1] the mechanism of this reaction consists in the formation of a primary radical I, which then rearranges to give II as is expressed below,



I II

[1] Ber., **53**, 370 (1920).

and the latter then polymerizes to form the dipyridyl derivative. The product dissociates again into the free radical when dissolved in certain solvents such as alcohol for example. These solutions possess a characteristic deep blue color, which disappears under the action of iodine:

$$2RNC_5H_5+I_2=2I\cdot(R)\cdot NC_5H_5$$

Sulphur radicals have been made the subject of an investigation by H. Lecher,[1] who has observed that colorless diphenyl disulphide, $C_6H_5S\cdot SC_6H_5$, dissolves in all indifferent solvents to give light-yellow solutions which become deeply colored upon heating. Moreover the substance melts to a yellow liquid which becomes colorless again upon solidification. Similar phenomena have been observed in the case of other sulphur compounds, and the question therefore arises as to whether this change in color is not due to the dissociation of the different substances into their corresponding free radicals. The fact that disulphides show a certain analogy in constitution to the hexaaryl-ethanes and the tetraaryl-hydrazines makes it seem probable that such is the case. This reaction cannot, however, be followed colorimetrically and the chemical relationships do no more than point to a weakening of the linkages between the sulphur atoms under conditions which might in themselves be sufficient to account for a change in color. For example, diphenylsulphide and *p*-dimethylanilino-disulphide combine with metals according to the equations:

$$C_6H_5\cdot S\cdot S\cdot C_6H_5+2Na=2C_6H_5\cdot SNa$$

$$(H_3C)_2N\cdot C_6H_4\cdot S\cdot S\cdot C_6H_4N(CH_3)_2+2Na=2(H_3C)_2NC_6H_4\cdot SNa$$

The second of these two substances also adds triphenylmethyl to give 1-dimethylaminophenyl-4 triphenylmethyl sulphide:

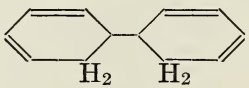
$$(H_3C)_2N\cdot C_6H_4\cdot S\cdot S\cdot C_6H_4\cdot N(CH_3)_2+2(C_6H_5)_3C=$$
$$2(H_3C)_2NC_6H_4\cdot S\cdot C(C_6H_5)_3$$

In conclusion it may be pointed out that the conception of the independent existence of free organic radicals is a conception which has been completely abandoned by chemists for almost a century. It may be recalled that in the time of Liebig the conception of a radical included the possibility of its actual existence, but that when all attempts to isolate free radicals failed, the word came to signify nothing more than an atomic complex which remained unchanged during the course of

[1] Ber., **48**, 524, 1425 (1915); also "Untersuchungen über aromatische Disulfide," Hans Lecher, Munich, 1920.

chemical reaction. It seems obvious at the present time that those chemists who sensed the truth most clearly were those who believed that radicals were not only actually capable of maintaining an independent existence but that they also possessed great chemical reactivity. On these grounds it is easy to understand why so few radicals have as yet been isolated since they must be imagined as forced by their very nature into combinations with other atoms or groups of atoms or even into combinations with each other.

H. Wieland limits the conception of free radicals to "free unsaturated complexes which are atomic in character and in which at least one component exhibits an abnormal valency." Radicals differ from *ions* since the latter conception carries with it the idea of an electric charge. While at the present time only a few chemists assume the existence of free radicals in interpreting chemical change it seems probable that this conception must in the future come into more and more general use and open the way to a freer, but at the same time more exact exposition of the mechanism of chemical transformations. While it may be said that explanations of this kind have been applied frequently in the past in interpreting the most varied chemical processes, an important difference between the old and the new method is to be found in the fact that in the past such explanations have not seemed capable of experimental verification. Such experimental verification is obviously essential to correct thinking since even in cases where the formulation of a reaction appears to point most decisively to the formation of free radicals as intermediate products, the greatest caution must be exercised before such a conclusion can be accepted. It must be remembered, too, in this connection that the actual existence of free radicals is at best very difficult to demonstrate experimentally since new methods must be worked out in each individual case. According to H. Wieland [1] explanations of this kind are open to many sources of error. For example, the synthesis of ethane from methyl bromide by the action of sodium, and the formation of diphenyl from benzene by the action of heat, would seem at first to depend upon the polymerization of the free radicals CH_3 and C_6H_5 which might be supposed to form as intermediate products during the course of these respective reactions. There are, however, other explanations of these phenomena which are equally plausible. For instance benzene itself might polymerize to dihydrodiphenyl:



[1] Ber., 48, 1098 (1915).

and the splitting off of hydrogen might then follow as a secondary reaction. And again in the synthesis of ethane it might be supposed that instead of a free methyl radical, a very reactive sodium compound is formed as the intermediate product in the reaction.[1] Good reasons for rejecting these and other possible interpretations of such reactions must obviously be found before an explanation which is based upon the assumption of free radicals can unreservedly be accepted.

It may be added that in the case of the benzidine rearrangement and of the analogous Fischer-Hepp rearrangements of diarylnitrosamines into *p*-nitrosodiarylamines, Wieland [2] would exclude any explanation which presupposes a dissociation of the respective substances into the free radicals C_6H_5NH— and $(C_6H_5)_2N$. As an argument against such an assumption in the case of the first type of transformation Wieland reasons that if tetraphenyl-hydrazine, which undergoes the benzidine rearrangement as readily as hydrazobenzene, actually dissociated into the free radical $(C_6H_5)_2N$, no diphenylbenzidine could possibly be formed. In the second case he argues simply that —NO and $(C_6H_5)_2N$— cannot be made to combine to give *p*-nitrosodiphenylamine.

[1] Am. Chem. Jour., **29**, 588 (1903); Ber., **48**, 1100 (1915).
[2] Ber., **48**, 1100 (1915).

CHAPTER XVI

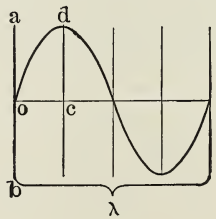
THE RELATIONSHIP BETWEEN COLOR AND CHEMICAL CONSTITUTION

When white light passes through a prism it is broken up into waves of different lengths corresponding to the colors red, orange, yellow, green, blue, indigo, violet. This is due to the fact that light of different wave lengths suffers different degrees of refraction in passing from a less into a more dense medium. For example light of the Frauenhofer line A in the red, which has a wave length equal to 0.00076 mm., suffers least refraction, while that of H in the violet which has a wave length equal to 0.000393 mm. suffers the greatest refraction. All of the different kinds of light are transmitted through the air at approximately the same velocity because of wave motions in the ether.

If during the transmission of light by transverse wave motion a given particle, such as an electron, an ion, etc., moves from o to a, back again to o, from o to b and back to o, it is said to have performed a complete oscillation. The time required for a complete oscillation is spoken of as a period (T) while the distance traversed by the wave during this time is referred to as a wave length λ. The reciprocal of T (or τ) represents the number of oscillations and the frequency v, the number of oscillations in 2π seconds. This may be expressed by the equation:

$$v = \frac{2\pi}{\tau}$$

The amplitude of an oscillation is measured by the distance between the position of equilibrium of a given particle and the position furthest from this which is assumed by the particle in any given swing. This is represented by the line cd in the accompanying diagram.



Different colors correspond to light of different wave lengths which are usually measured in terms of micro-millimeters, $\mu\mu$:

$$1\ \mu\mu = 0.000001\ \text{mm.} = 10^{-6}\ \text{mm.}$$

Light waves are also measured in terms of Ångstrom units—:

$$1\ \text{Å} = 10^{-7}\ \text{mm.} = 10^{-8}\ \text{cm.}$$

The reciprocal of this value, which equals the number of oscillations to 1 mm., is used in graphic representations. For example, the D line for sodium light has a wave length of 0.0005892 mm. = 589.2 $\mu\mu$ = 5892Å. The number of oscillations is $\frac{10^7}{5892} = 1697$ to 1 mm. The wave length of Frauenhofer's line A in the red equals 0.00076 mm., or 760 $\mu\mu$, and that of the line H in the violet 0.000393 mm., or 393 $\mu\mu$,—these values marking the limits of the visible spectrum. White light is, however, made up of other rays in addition to these which, although they cannot be perceived by the eye, may be measured indirectly. These rays lie beyond the regions of the red and the violet and are, therefore, referred to as the infra-red and the ultra-violet respectively. Regions of the spectrum which correspond to the following series of wave lengths:

infra-red rays = 0.06 − 0.00076 mm.	visible rays = 0.00076 − 0.0004 mm.	ultra-violet rays = 0.0004 − 0.0001 mm.

have been more or less carefully investigated. A consideration of these figures clearly demonstrates that visible rays constitute only a relatively small fraction of the total spectrum. This fact has not always been fully recognized in the past and as a result somewhat misleading conceptions in regard to absorption phenomena have been current.

If ordinary white light is allowed to pass through colored bodies or colored solutions, certain rays are absorbed while those which pass through unchanged give a characteristic color to the body or solution. If, for example, red is absorbed the substance will appear blue-green. In other words, red and blue-green are complimentary colors and when mixed together give the effect of white light. If, on the other hand, light which has passed through a colored substance is resolved into its component colors by means of a prism, it will be found to lack certain colors. The spectrum which is obtained in this way is called an absorption spectrum, the absorption being referred to as unilateral if it takes place in only the blue or the red respectively, and bilateral if it occurs

in both regions. An absorption spectrum is said to be banded if dark bands are formed as the result of absorption.

Many substances which appear to be colorless have been found to possess absorption spectra. In such cases absorption takes place in the region of the infra-red or of the ultra-violet and not in the region of the visible spectrum. Benzene, for example, although it is apparently an absolutely colorless substance, possesses a very complicated absorption spectrum which may be readily detected by means of the photographic plate. In a strictly scientific sense benzene should, therefore, be regarded not as a colorless but as a definitely colored compound.

Absorption relationships in ultra-violet have been very carefully studied by W. N. Hartley.[1] These investigations have been of value because they have served to throw new light upon many of the problems of organic chemistry. Hartley found, for example, that aromatic compounds such as benzene and its derivatives, pyridine, pyrazine, etc., exhibit selective absorption while derivatives of the fatty hydrocarbons, on the other hand, usually show continuous absorption. Certain exceptions to the latter statement are to be found, however, among the ketones, diketones and similar substances, all of which possess strongly banded absorption spectra.

While benzene absorbs in ultra-violet and appears colorless, nitrobenzene and aniline absorb within the limits of the visible spectrum and appear light yellow in color. This seems to indicate that the substitution of the hydrogen of benzene by NO_2 or NH_2 respectively tends to shift the absorption bands of the substance from the invisible region into the visible region of the spectrum. If such an assumption is correct it should be possible to reverse this process and to shift absorption in the opposite direction, viz., from infra-red → red → violet → ultra-violet. This can in fact be accomplished.

Within the limits of the visible spectrum changes in color from yellow → orange → red → blue → violet are referred to as a " deepening color " and are supposed to be brought about by the action of so-called *bathochrome* groups, while changes in the opposite direction are said to " lighten the color " and are brought about by so-called *hypsochrome* groups.[2]

In order to explain the emission and absorption of light Ångstrom made the assumption in 1855 that a definite analogy existed between the phenomena of light and sound. He supposed that the same theory which interpreted resonance as due to the reinforcement of a particular

[1] Jour. Chem. Soc., **53**, 641 (1888); **73**, 695 (1898); **77**, 846 (1900).

[2] H. T. Bucherer, "Lehrbuch der Farbenchemie," Leipzig, 1914, p. 245; H. Kauffmann, "Valenzlehre," 1911, p. 433; Urbain, Compt. rend., **157**, 594 (1913).

sound, might be applied to explain absorption. In the latter case a ray of given wave length might be assumed to be neutralized by the movements of molecules or atoms which possessed the same period of vibration.

According to the electro-magnetic theory of light the relation between emission and absorption is explained by supposing that light waves possess the power of exciting the electrons of the atoms to movements which are electrical in character. These oscillations of electrons may be such that energy is radiated in all directions, in which case general absorption takes place. In order to account for selective absorption the further assumption is made that in such cases the electrons are more readily affected by certain vibrations than by others. In this way waves of light which have approximately the same periods of oscillation as the electrons are damped or absorbed.

J. Stark assumes that valence fields are present on the atoms and that these oscillate about positions of equilibrium which have their centers at points somewhere between the negative electrons and the positive zones on the surface of the atoms. The vibrations of these valence fields depend upon simultaneous movements of the electrons which may or may not be accompanied by oscillations of the atoms themselves. The vibrations of the valence fields of the chemical atoms are assumed to be electro-magnetic in character, and may be accompanied by either the emission or absorption of light. It follows that only those rays of light which possess the same frequencies as the valence fields of the chemical atoms will be absorbed and that the measurement of the absorption of a given compound therefore affords a means for determining the character of the valence fields which are present on its atoms.

Stark makes the further assumption that the valence electrons which are present on or above the surface of the atom represent the centers of the so-called band spectra. This assumption is based upon a systematic study of the oscillation of particular valence fields in the case of individual atoms (monatomic gases) and also in the case of molecules, within and without the influence of intermolecular unions. As a result of this investigation it was possible to draw certain fairly definite conclusions in regard to the character of the vibrations of the valence fields of electrons alone or of atoms and groups of atoms alone, or of valence electrons coupled with atoms, etc. The reader must be referred to Stark's original presentation of the subject for a full description of the manner in which banded absorption may be brought about in the infra-red, in the ultra-violet and in the visible regions of the spectrum. For purposes of the present discussion the general statement must suffice

that under favorable conditions the characteristic behavior of every vibrating particle in a given molecule may be determined, and that as a result it has been discovered that the absorption spectrum of any chemical individual is compounded of a great number of separate parts which represent respectively the absorption of the different units present in the complex. According to Lifschitz, for example, the broad bands which are so frequently observed in connection with the spectra of organic compounds, actually consist of a series of fine single bands which follow each other so closely that they appear to merge. They may be regarded as corresponding to a series of individual resonators possessing frequencies which are approximately the same.

Since liquids and solids do not possess sharply defined absorption bands, it was impossible in the case of organic compounds, with very few exceptions, to study directly the influence of individual atoms upon the absorption spectrum of the molecule. Insight into atomic relationships in organic chemistry was, nevertheless, obtained indirectly from a study of changes in absorption which result from substitutions in given molecules. Here interest at first centered in the behavior of so-called chromophore and auxochrome groups because it was generally believed that the presence of such groups in a given molecule was sufficient to account for the phenomenon of color. Later the presence of certain characteristic bands in the absorption spectra of different substances came to be associated with a particular structure within the molecule and in this way it became possible to detect the presence of the benzene ring, the dicarbonyl grouping, the *enol-keto* grouping, etc. These observations served to establish a tentative relationship between the optical properties of a particular substance and the chemical constitution of its molecule, and marked the beginning of very important developments in the field of physical chemistry.

This branch of chemical science has gradually grown until at the present time the absorption spectra of organic compounds afford a much more accurate and minutely differentiated representation of the relationships which exist between the different atoms in the molecule than is afforded by structural or constitutional formulas. Indeed the means for expressing interatomic relationships have been so enlarged and enriched through a study of absorption phenomena that a direct measure of the strength of different forms of union between the atoms of a molecule is now possible. It must be added, however, that up to the present time the results which have been obtained by the application of optical measurements lack uniformity. This is due to the fact that no single method for the determination and graphic representation of absorption spectra has been found acceptable by all investigators. It follows that

any general comparison of the absorption spectra of different compounds is obviously open to error and that this situation will continue until a greater uniformity of method prevails. Various ways for determining the absorption spectra of organic compounds have been suggested by Hartley, Baly, J. Stark, Henri, Weigert, K. Schaefer and others and these may now be considered briefly.

If light of a definite intensity penetrates a solid body a fraction of its intensity is absorbed and the total intensity is thereby weakened. Intensity of light is also weakened in direct proportion to the depth to which it penetrates a given body. If during absorption all fields of light absorb more or less equally, absorption is said to be " continuous " but if certain regions are markedly weakened as compared with other adjacent regions, absorption is said to be " selective."

According to Lambert the intensity of light of definite wave lengths depends upon the relative thickness of the layers through which it passes viz.,

$$J = J_0 e^{-Kd}$$

where J_0 represents the intensity of light entering a body; J the intensity of light leaving the body; d, the thickness of the layer through which the light passes; e the base of the natural logarithms (2.71828); and K, a constant which depends upon the nature of the absorbing substance and upon the respective wave length of light.

It follows that the intensity may be kept constant if d varies inversely as the so-called coefficient of absorption, K. The expression may be rearranged to read

$$ln\frac{J_0}{J} = Kd \quad \text{or} \quad log\frac{J_0}{J} = kd\,^1$$

Moreover if $\frac{J}{J_0} = \frac{1}{10}$, it follows that $k = \frac{l}{d}$.

In accordance with these deductions Bunsen and Roscoe have called K the coefficient of extinction and, in the case of solids, defined it as the reciprocal of the value represented by a layer of such thickness that the intensity of light would be weakened by one-tenth in passing through it. In other words the coefficient of extinction is a measure of the strength of absorption, and may be represented by

$$log\frac{J_0}{J} = k \cdot d$$

In the case of solutions [2] the same general rule holds, assuming of course that the solvent itself does not absorb so that given a solution of

[1] $K = 2.3026\ k$.

[2] Ley, "Beziehungen zwischen Farbe und Konstitution," p. 59.

definite concentration absorption will depend upon the thickness of the layer through which light passes. In the case of solutions of different concentrations, on the other hand, Beer has discovered that absorption is proportional to the concentration, or

$$\epsilon = log\frac{J_0}{J} = k.\ c.\ d.$$

where c equals the concentration of a given solution. It follows that the same effect may be produced by changing the thickness of the layer and keeping the concentration constant, as by changing the concentration and keeping the thickness of the layer constant. In other words, the absorption will remain the same if the thickness of the layer through which light passes is inversely proportional to the concentration of the solution. Thus a layer of a given concentration is equal to another of double the thickness and one-half the concentration. This is known as Beer's law and methods of colorimetry and spectro-analysis are founded upon it.

While Beer's law holds in a great number of instances, certain important exceptions have been observed which are of interest because they help to elucidate the chemical nature of solution. It seems probable that Beer's law holds in every case where the composition of the substance is unchanged by solution.[1] If, however, polymerization occurs as of $A_n \rightleftarrows nA$ or dissociation as of $AB \rightleftarrows A'+B'$, or if the particular solvent affects the condition of equilibrium in a chemical system so that changes in mass take place, variations from Beer's law must result.[2]

J. Piccard [3] has investigated the phenomena of dissociation in solution from an experimental and also from a purely theoretical point of view and has formulated a so-called *colorimetric law* of dilution which combines the law of mass action and Beer's law. If a substance A dissociates in solution to form $a_1, a_2, \ldots a_n$ so that

$$A \rightleftarrows a_1+a_2+\ldots a_n$$

and if the molecular concentrations of these substances are equal to $C, c_1, c_2 \cdots c_n$ respectively, it follows that

$$\frac{C}{c_n} = Const.$$

If it now happens that dilution favors the formation of a_n, which is colored, at the expense of A which is colorless, it is obvious that the effect of dilution will be to decrease C more rapidly than c_n and the

[1] A. Hantzsch, Ber., **50**, 1414 (1917).

[2] Ber., **45**, 554 (1912); Ley, "Farbe und Konstitution bei Organischen Verbindungen," p. 61, Leipzig, 1911.

[3] Annalen der chemie, **381**, 347 (1911); also Hantzsch, Annalen der chemie, **384**, 135 (1911).

observed phenomena will therefore appear to deviate from Beer's law. It has been demonstrated experimentally by Piccard in the case of ethereal solutions of hexaphenylethane that the color of the solution becomes more and not less intense with successive dilutions until at very great dilutions it is orange-yellow. In this case dilution obviously favors the formation of triphenylmethyl:

$$\underset{\text{Colorless}}{(C_6H_5)_3C\cdot C(C_6H_5)_3} \rightleftarrows \underset{\text{Yellow}}{2(C_6H_5)_3C}$$

Wieland [1] has been able to point out quite recently that in the case of hexaphenylethane in solution in benzene it may be demonstrated experimentally that the substance on dilution obeys both the law of mass action and Beer's law. Supposing that the experiment is conducted with great care under the proper conditions, it will be observed that in the first second after dilution the color of the solution becomes paler and almost seems to disappear. It thus obeys Beer's law and suffers a loss of color proportional to dilution. Immediately following this, however, a deepening of color takes place and the solution becomes bright yellow. This change is due to the establishment of a new condition of equilibrium and indicates the presence of a mixture in which the concentration of the colored component (c_n) is greater than that of the colorless component (C).

It is obviously possible to apply Beer's law with a view to determining whether a colored substance suffers a change in constitution upon solution. If, for example, a substance is dissolved in a given solvent and the intensity of its absorption in that solvent is determined before and after dilution, it follows that if it is found to obey Beer's law exactly no change in its constitution can have occurred. Such determinations are valuable because by means of them it is possible to follow the effect of solution, temperature,[2] etc., upon the chemical constitution of colored compounds.

In order to define the color of a substance exactly it is necessary to know what fraction of light of a specific wave length it absorbs under a given set of conditions. After this has been determined in as many different fields of the spectrum as possible and the relation of the substance to light of different wave lengths established, an exact conception of its power of absorption is obtained.

Two general methods for the measurement of absorption are in use. The first consists in determining the extinction coefficient,—or, in the case of solutions, the molecular extinction,[3]—in as extended a field

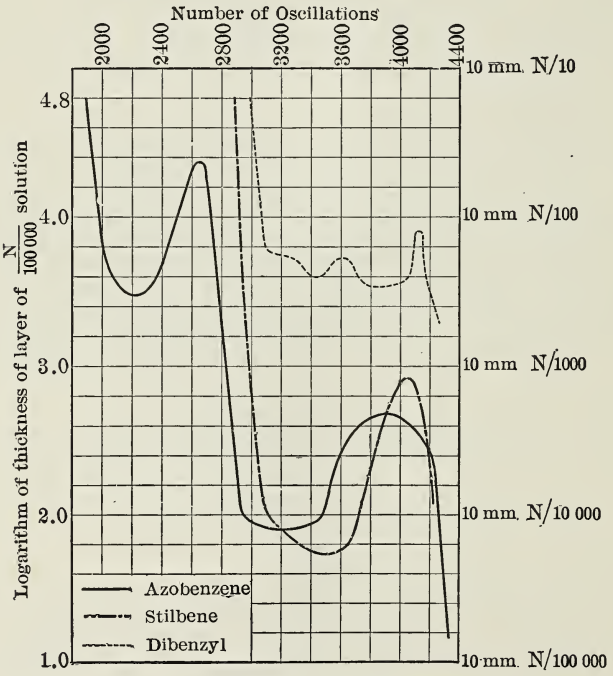
[1] Ber., **48**, 1097 (1915).

[2] Compare K. Schaefer, Zeitschr. angew. Chemie, **33**, 26 and following (1920).

[3] $\text{Molecular Extinction} = \dfrac{\text{Coefficient of Extinction}}{\text{Concentration}}$.

of the visible spectrum as possible. This method is very exact but is limited in its application to substances absorbing within the field of the visible spectrum. The second method is less exact but much more general in its scope. It has been developed by Hartley [1] and is in current use in the case of all determinations which involve solutions. Hartley's procedure is to dissolve the molecular weight of the substance expressed in milligrams in a known volume of solvent and to photograph the spectrum in layers of decreasing thickness at definite intervals, say of 1 mm. When a final thickness of 1 mm. has been reached the solution is diluted to a definite strength, and the process repeated until the solution reaches a state of such dilution as to be non-absorbent. The results are set forth by plotting the oscillation frequencies of the limits of the absorption bands against the logarithms of the respective thicknesses of the layers.[2] When the points obtained in this way are joined, the absorption curve or a curve showing the molecular vibrations, of the substance is formed.

The following illustration shows the appearance of such a curve: [3]



[1] Jour. Chem. Soc., **47**, 685 (1885).
[2] Jour. Chem. Soc., **85**, 1029 (1904).
[3] Ber., **43**, 1189 (1910).

By the application of these methods the absorption of a great many substances has been measured and as a result the optical effect of the presence of different groups in the molecule has been determined with great exactness.[1] Moreover a comparative study of the absorption spectra of different substances aids in the interpretation of their structural relationships. For example, Hantzsch recently discovered a new absorption spectrum for nitro-compounds, with the result that it is now thought that nitro-groups may be present in organic molecules in any of three different forms of combination, each of which possesses a characteristic absorption spectrum. These are differentiated as true nitro-groups (NO_2), aci-nitro groups (O=N-O—), and the new so-called "conjugated aci-nitro groups."[2]

The results which are obtained by use of the Hartley-Baly method are, however, frequently very misleading, as J. Bielecki and V. Henri and also F. Weigert have recently demonstrated,[3] and it has therefore been urged that this method be abandoned in favor of one which is more exact.[4] The substitute which has been suggested by J. Bielecki and Henri consists in the quantitative determination of absorption of ultraviolet by the photometric comparison of the intensity of different lines of definite wave lengths after these lines have passed through layers of different thickness of the solution to be investigated. For exact details in regard to procedure the reader is referred to the original paper.[5] The curves which serve as a graphic representation of the phenomena are plotted upon abscissas which represent either the wave length (λ) or the oscillation frequencies per second ($v \times 10^{-12}$), and on ordinates which represent molecular absorptions ϵ, as calculated on the basis of

$$J_0 = J 10^{\epsilon c d}$$

where c equals the molecular concentration and d the thickness of the layer in centimeters. In some of the more recent work *log* ϵ has been substituted for ϵ.[6]

A somewhat simpler method, which is applicable to the determination of absorption in the visible spectrum has been suggested by F. Weigert. It depends upon a comparison of the absorption of the sub-

[1] Stobbe, Annalen der Chemie, **349**, 364 (1906); **370**, 93 (1909); Ber., **39**, 293, 761 (1906); also Martens and Grünbaum, Drudes Annalen, **12**, 984 (1903); Hantzsch, Ber., **39**, 4153 (1906).

[2] Ber., **45**, 85 and 553 (1912).

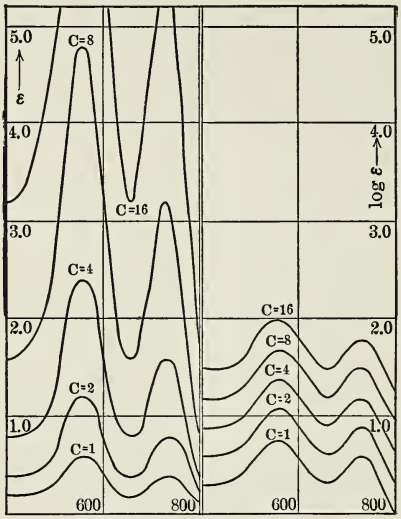
[3] Ber., **46**, 3628 (1913); **49**, 1496 (1916).

[4] Ber., **45**, 2819 (1912); **46**, 1304, 2596, 3627, 3650 (1913); **49**, 1496 (1916).

[5] Physikal. Zeitschr., **14**, 151 (1913); Ber., **46**, 1306 (1913).

[6] Ber., **46**, 3631 (1913).

stance whose structure is in doubt with a substance of known constitution (the so-called normal substance), supposing of course that both contain certain lines of the same wave length. For the practical carrying out of this experiment the reader must again be referred to the literature on the subject.[1] Weigert's so-called typical color curves are plotted on abscissas which represent either the wave lengths (λ) or the oscillation frequencies (v) and on ordinates which represent the logarithms of the extinctions. The curves shown in the accompanying figures serve to illustrate how much more apparent variations become when the successive curves are plotted on *log* ϵ instead of ϵ.



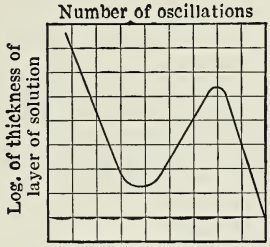
Curves plotted for different concentrations possess the same general form and this is also true if the layers are of different thickness or if different units are used in representing the abscissas and the ordinates. In every instance curves which are characteristic of the absorbing substance are obtained.

The disadvantages and misconceptions connected with the methods which have thus far been considered and the complications which arise because of the absorption of the solvent, may be avoided by using a method which has recently been worked out by K. Schaeffer and A. Hardtmann.[2] The apparatus is relatively simple and permits the deter-

[1] Ber., **49**, 1530 (1916).

[2] Zeitschr. angew. Chemie, **33**, 25 (1920); also compare Zeitschr. wiss. Phot., **8**, 212 (1910); Zeitschr. anorg. Chemie, **97**, 285 (1916); **98**, 70, 77 (1916); Zeitschr. wiss. Phot., **17**, 193 (1918); Zeitschr. anorg. Chemie, **100**, 249 (1917); **104**, 212 (1918); Zeitschr. physikal. Chemie, **93**, 312 (1919).

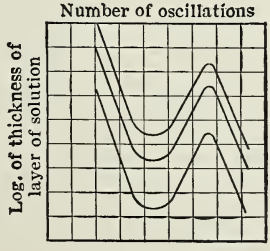
mination of comparatively exact extinction measurements even in the region of the extreme ultra-violet. The so-called extinction or absorption curve is drawn by plotting either the wave lengths or the number of oscillations as abscissas against the logarithms of the thickness of the layers of the solution as ordinates. If curves are plotted for solutions of different concentrations, these curves will either all coincide, in which case it may be assumed that Beer's law holds since the absorbing complex is unchanged upon dilution, or, the position of the curves may be



different so that they no longer coincide, in which case it may be assumed that dilution is accompanied by changes in equilibrium in the chemical system, as for example,

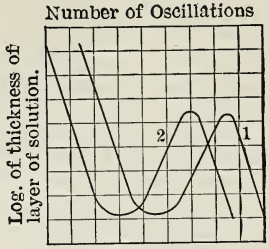
$$A \text{ (colored)} \rightleftarrows B \text{ (colorless)}.$$

Under these circumstances the curves plotted for different concentrations of solution may be similar in form but suffer a vertical displacement. The accompanying figure illustrates such a condition, the degree of vertical displacement serving to measure the change in the concentration of A.

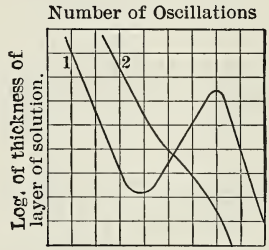


In certain instances the curves plotted for different concentrations show a horizontal displacement in which case it is usually assumed that the two substances, A and B, are structurally identical but differ

in the strength of the affinities which operate between the different atoms. Such a relationship is illustrated in the following figure:



Finally in cases where the change $A \rightarrow B$ involves a complete change in the chemical constitution of the substances, curves plotted for different concentrations of solution will exhibit marked differences in form as well as is position. Such a relationship is shown by the curves in the following figure:



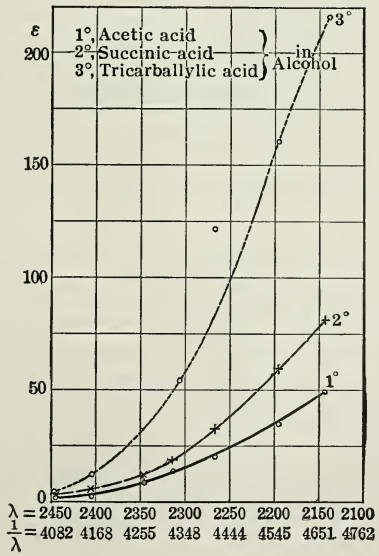
This method may be applied to determine the extent to which two substances interact. For this purpose two curves representing the two substances respectively are plotted one behind the other, and this figure is then compared with a curve plotted for a mixture of the two substances. Such a comparison will readily show whether or not a reaction between the two substances has taken place. Conclusions may also be drawn in regard to the relative conditions of equilibrium in the reaction product.

A number of more or less important rules have been formulated in regard to the relation which exists between the chemical constitution of organic compounds and their absorption curves. For example, V. Henri and J. Bielecki have constructed absorption curves for a large number of alcohols, acids, esters, aldehydes, and ketones in order to ascertain by means of systematic comparisons the way in which absorption depends upon the differences in atomic groupings within the molecule. The results of these experiments seem to indicate that minute differences in chemical constitution may be detected by means of a comparative study of absorption curves and that phenomena in this field

are open to a numerical treatment in much the same manner as in the case of refractions. While the problem is still in the process of development and is not always treated in a consistent way even by one and the same investigator, certain more or less definite conclusions have, nevertheless, been arrived at which are of interest and which may be considered briefly.

A comparative study of the absorption curves of homologous aliphatic alcohols, acids, esters, etc., has resulted in the formulation of a number of important rules in regard to the effect of substitutions upon absorption spectra. The addition of CH_2, for example, is always accompanied by (1) a shifting of the absorption band of the substance in the direction of of the red, and (2) an increase in the height of the curve at the point of maximum absorption. In the case of substances having the general formula $C_nH_{2n+1}\cdot COOR$, where R represents an alkyl group, it has been found that absorption depends largely upon the value of n in the residue C_nH_{2n+1} and is only very slightly influenced by the nature of R. The carboxyl residue, COO, on the other hand seems to have a very marked effect upon the absorption as is obvious from a comparison of the absorption curves of mono-, di-, and tri-basic acids, such as, for example, acetic, succinic, and tricarballylic acids:

$$\begin{array}{l} CH_3 \\ | \\ COOH \end{array} \qquad \begin{array}{l} CH_2\text{——}CH_2 \\ | \quad\quad | \\ COOH \quad COOH \end{array} \qquad \text{and} \qquad \begin{array}{l} CH_2\text{——}CH\text{——}CH_2 \\ | \quad\quad | \quad\quad | \\ COOH \quad COOH \quad COOH \end{array}$$



Of these acids the last two may be regarded as respectively doubling and trebling the CH_2COOH grouping which is present in acetic acid and they should therefore be expected to show a proportional increase of absorption from left to right. As a matter of fact it has been observed, however, that while the absorption curves of these three acids are similar, the relative increase in absorption is not proportional to the number of carboxyl groups but is so much stronger as to suggest a definite exaltation in optical properties. Under such circumstances absorption cannot be regarded as simply additive in character, as is the case in refraction, but it must be clearly recognized as *composite* and as representing not merely the individual additive effects of different chromophore groups but also the increase and decrease in exaltations which result from the mutual interactions of these groups upon each other. This conclusion is very important in connection with the development of a quantitative relation between absorption and constitution and will be considered again in some detail later in this chapter.

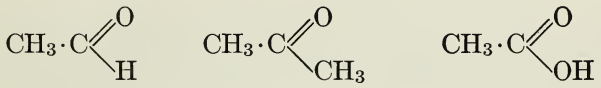
The absorption curves of saturated mono-, di-, and tri-basic acids have been found to resemble these of the corresponding hydroxy acids very closely. In fact the introduction of alcoholic hydroxyl into a molecule of acid seems to produce only a very slight exaltation in the absorption of the substance. In comparing saturated and unsaturated acids it has been observed that the latter differ from the former in that they possess a much stronger absorption in the region of the ultra-violet. It may be said in general that the presence of unsaturated ethylene linkages causes relatively greater exaltations in absorption than is produced by the presence of carbonyl, but a comparison of different unsaturated acids shows that the degree of exaltation in any given case depends upon the relative proximity of these two groups. Acids belonging to the acetylene series also absorb ultra-violet rays more strongly than the corresponding saturated acids, and here again the exaltation seems to depend upon the relative proximity of the triple bond to the carbonyl group.

Stereoisomers such as the dextro and lævo tartaric acids, fumaric and maleic acids, mesaconic and citraconic acids, possess different absorptions. The only rule which can be formulated in regard to them is that in the case of geometrical isomers the *trans*-modification is apt to absorb more strongly than the *cis*-modification.

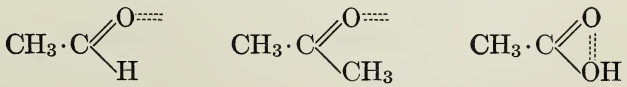
A study of saturated aldehydes and ketones reveals the fact that both possess characteristic absorption bands between $\lambda = 2800\ \mu\mu$ and $\lambda = 2700\ \mu\mu$. In the case of the simplest aldehydes the height of the curve at maximum absorption is relatively low but it is observed to rise regularly as the number of CH_2 groups is increased. Unsaturated aldehydes

and ketones show exaltations in their absorptions as compared with the corresponding saturated compounds and, as in the case of unsaturated acids, the degree of exaltation depends upon the relative proximity of the ethylene and carbonyl groups. The absorption curves of the majority of aldehydes and ketones are characterized by minimum absorptions in the region of the shorter wave lengths immediately to the right of the point whose relative height seems to depend upon the relative complexity of the alkyl residue (being highest in the case of those substances which are most complex). Acetone represents an exception to this general rule since it does not show the characteristic minimum absorption in the shorter wave lengths up to $\lambda = 2144\ \mu\mu$.

A comparison of the absorption curves of corresponding acids, aldehydes, and ketones,

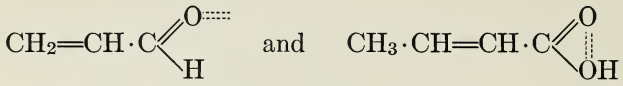


shows that they apparently bear no resemblance to each other and it must, therefore, be concluded that the replacement of hydroxyl by hydrogen or by alkyl so completely alters the constitution of the molecule as to produce a fundamental change in the general absorption of the substance. This observation is not in harmony with the structural formulas which are generally accepted as representing the atomic relationships of these three classes of substances and which assume the presence of a carbonyl group as common to all. If carbonyl is actually present in acids it is difficult to understand why these substances do not possess the absorption bands which are so characteristic of aldehydes and ketones and which have been interpreted as due to the presence of a carbonyl group in the molecule. The substitution of hydrogen or of alkyl by hydroxyl is not in itself sufficient to account for this, since in the case of other classes of compounds substitutions of this type produce relatively slight changes in absorption. It would therefore seem to follow that the old formulas do not adequately express the actual chemical relationships which exist in the case of these three classes of substances, and Henri and Bielecki propose the following substitutes:



These investigators agree with Lowry and Southgate in believing that acids differ radically from aldehydes and ketones in their chemical constitution and they suppose that these differences may be satisfactorily

accounted for on the basis of differences in saturation. In the case of acids, for example, the partial valencies on the oxygen of the carbonyl group are assumed to be saturated while in the case of aldehydes and ketones they remain unsaturated. These assumptions find further confirmation in the optical properties of unsaturated aldehydes and ketones. The formulas for acrolein and α-crotonic acid for example must be corrected to

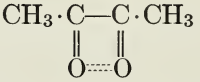


since, while both substances have been observed to possess strong exaltations of absorption, only the former shows the particular bands which characterize the presence of carbonyl.

A similar explanation applies to diacetyl, which exhibits a much weaker absorption than might be expected from the fact that it contains two carbonyl groups and from the additional fact that acetonylacetone,

$$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$$

possesses an absorption constant which in maximum is eight times greater than that of acetone. Such abnormal behavior on the part of diacetyl is intelligible only on the assumption that partial valencies on the oxygen atoms of the two adjacent carbonyl groups mutually saturate each other:



When Henri and Bielecki [1] discovered that the mutual interaction of two chromophore groups which are present in the same molecule corresponds to hypsochromic and hyperchromic changes in absorption they made this observation the basis for the formulation of a method by which it is now possible to calculate the absorption curve of a compound of known structure. The particular observation was to the effect that if two chromophore groups occupy conjugate positions with reference to each other they produce a weak hyperchromic and a strong hypsochromic effect while if, on the other hand, the two groups are widely separated in the molecule the opposite effect is observed. In the latter instance the interaction of the two chromophore groups will tend to increase the height of the absorption curve (hyperchromic effect) while the shifting of absorption in the direction of longer wave lengths (hypsochromic effect) will be negligible.

[1] Ber., **47**, 1690 (1914).

According to this observation the absorption constant, ϵ, must be regarded as composite and must be assumed to represent not merely the additive effects of the different chromophores but also the effect of their interaction upon each other inside the molecule. Henri and Bielecki [1] were then able to demonstrate that the absorption curves of acetone, acetic acid and other monobasic aliphatic acids may be represented by means of three characteristic constants which are interdependent and whose relation may be expressed either by the Ketteler-Helmholtz-Drude equation:

$$\epsilon = \frac{a\lambda^2}{(\lambda - \lambda_m{}^2) + g^2h^2}$$

or by the Henri-Bielecki exponential formula:

$$\epsilon = \alpha \cdot \nu \cdot e^{-\beta(\nu - \nu_0)^2}$$

In the first equation α, g^2 and λ_m represent the three characteristic constants and in the case of carbonyl for example have the value $\alpha = 2.57 \times 10^6$, $\lambda = 2721$, and $g^2 = 1.63 \times 10^{-5}$. In the second equation ϵ represents the absorption constant for the frequency ν, while α, β and ν_0 represent the characteristic constants. As their name implies these constants possess different values in the case of every chromophore. It follows that if the characteristic constants are known the value ϵ for any given frequency may be calculated and in this way the absorption curve of a compound of known structure may be predicted.

If the two chromophore groups are present in a molecule the hypsochromic and hyperchromic effect will vary depending upon their relative positions. Under such circumstances the absorption curve of the substance may be determined by means of the following equation:

$$\epsilon = n \cdot \alpha_1 \cdot \nu \cdot e^{-\beta_1(\nu - \nu_1 - \Delta\nu^2)} + n \cdot \alpha_2 \cdot \nu \cdot e^{-\beta_2(\nu - \nu_2 - \Delta\nu)^2}$$

in which $\nu_1\alpha_1\beta_1$, and $\nu_2\alpha_2\beta_2$ represent the characteristic constants of the two chromophores; n, the factor of hyperchromism; and $\Delta\nu$ the factor of hypsochromism. If the chromophores are present in conjugate systems n is small and $\Delta\nu$ is large, while if the two groups are in isolated positions this relation is reversed.

In summing up the work of Henri and Bielecki it must be stated that while these investigators are of the opinion that the formulation of the above relationships has made a numerical treatment of absorption possible and affords a means for calculating the values for absorption constants in much the same way as in the case of refractions, the evidence upon which their conclusions are based is distinctly controversial in character. The objections which have been brought forward

[1] Physikal. Zeitschr, **14**, 516 (1913).

by Lifschitz [1] while they cannot be reviewed in detail in the present treatise are, nevertheless, of serious importance.

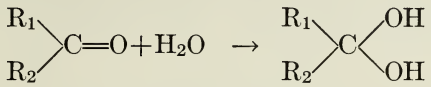
An extended study of absorption phenomena in the field of organic chemistry has led A. Hantzsch [2] to recognize that the interaction of the solvent and the solute may produce one or the other of the following effects:

I. The absorption of the substance may be radically changed in which case the absorption curve assumes an entirely different form. Under these circumstances alterations in the chemical constitution of the substance may be supposed to have taken place. Such alterations represent changes in the distribution of affinity and may involve either the principal or the partial valencies present on the atoms. Reactions which may be assumed to result directly from the action of the solvent are exemplified in rearrangements from *keto* to *enol* modifications, from nitro- to aci-compounds, from colorless to yellow dioxyterephthalic esters, from colorless to polychromic salts of the oximidoketones, from colorless to yellow pyridonium salts, etc. In these cases the change is not supposed to be catalytic in character but to depend upon differences in the stability of the solvates which are formed by the addition of the solvent to one or the other modification of the solute. II. The absorption of the substance may not be materially changed in which case the form of the absorption curve will remain the same while its position may either be the same or may be shifted slightly. Under these circumstances no appreciable chemical change is assumed to have taken place, although this does not preclude the formation of unstable addition products between molecules of the solute and solvent. Trinitrotriphenyl carbinol, $(C_6H_4NO_2)_3COH$, for example, reacts with almost all solvents to give solid heterogeneous products of association. Of these $(C_6H_4NO_2)_3COH \ldots CH_3OH$ and $(C_6H_4NO_2)_3COH \ldots CHCl_3$ possess identical absorption curves within the limits of experimental error.

From a chemical point of view all solvents may be regarded as liquids which are able to form either relatively stable homogeneous association products (solvates) or heterogeneous association products with the dissolved substance. Solvents have the power of inducing rearrangements in the case of isomeric and tautomeric compounds because the equilibrium relationships of stable and meta-stable modifications are frequently different from those of the corresponding solvates. In certain instances the presence of even a trace of solvent may be sufficient to cause the isomerization of substances in the solid state.

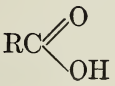
[1] Zeitschr. wiss. Phot., **16**, 149 (1916).
[2] Ber., **50**, 1413 (1917).

Solvents also have the power of entering into actual chemical combinations with the dissolved substance. Here the reaction may result from the saturation of either partial or principal valencies. An example of the latter type of combination is to be found in the formation of certain hydrates such as:



In these cases the form of the absorption curve is radically changed.

As the result of a very exhaustive study of absorption A. Hantzsch has discovered the existence of very fine differences in the properties of organic acids and their derivatives. On the one hand Hantzsch compared the absorption of salts of the alkali and alkali earth metals with the absorption of the corresponding acids. These measurements were made in the ultra-violet region of the spectra and the resulting pairs of curves were found to be identical in all respects. When, on the other hand, the absorption of the esters of these acids was determined it was found that although different esters of the same acid gave identical absorption curves, these curves were markedly different from the curves of the corresponding free acid or of its salt. In general it was observed that the esters showed a much stronger absorption than the corresponding salt. While absorption in every case has been found to depend both upon the nature of the acid and of the solvent, it may be said in general that the absorption of a given acid stands approximately midway between the respective absorptions of its salts and esters. Trichloracetic acid, for example, possesses an absorption as weak as that of its salts when examined in solutions of water or petroleum ether, while in solutions of alcohol and ethyl ether it absorbs just as strongly as its esters. Hantzsch is of the opinion that differences in optical properties in these and other similar instances cannot be accounted for on the basis of associations or dissociations in solution and that they may, therefore, be assumed to correspond to actual differences in the chemical constitution of the substances. In other words, in so far as it is possible to ascertain under the conditions of Hantzsch's experiments, all the evidence tends to support the conclusion that the differences in absorption which have been observed in the case of acids, esters and salts are due to differences in the structure of these substances. Moreover a close study of the formula



shows that although it has been generally accepted as representing the constitution of organic acids, it fails to account for the distinctly acid character of the hydrogen of the hydroxyl group as compared with that of the hydrogen which is present in the hydroxyl groups of alcohols. The very strong tendency towards dissociation which particularly distinguishes acid hydrogen is much more readily accounted for on the basis of Werner's coordination formula:

$$R\cdot C\left.\begin{matrix}O\\O\end{matrix}\right\}H$$

since this represents the hydrogen atom as occupying a position in the outer or dissociable zone with respect to the central carbon atom. The dissociation of metallic atoms may be explained by means of analogous formulas

$$RC\left.\begin{matrix}O\\O\end{matrix}\right\}H \quad \text{and} \quad RC\left.\begin{matrix}O\\O\end{matrix}\right\}M$$

or

$$RCO_2 : H \quad \text{and} \quad RCO_2 : M$$ [1]

Since acids lose their power to dissociate hydrogen when dissolved in certain solvents and under these conditions are optically different from the corresponding dissociable modification, Hantzsch assumes that changes in constitution have occurred which involve the formation of a pseudo-acid. Moreover since these pseudo-acids are optically identical with the corresponding esters Hantzsch assumes that they have an analogous structure which he represents by the use of the older formulas:

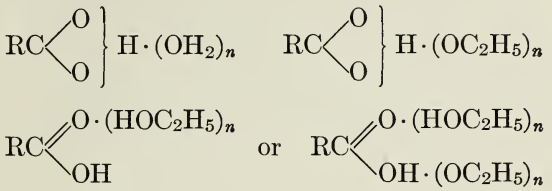
$$RC\begin{matrix}\diagup\!\!\!\diagup O\\ \diagdown OH\end{matrix} \quad \text{and} \quad RC\begin{matrix}\diagup\!\!\!\diagup O\\ \diagdown OR\end{matrix}$$

According to this conception trichloracetic acid would have the formula $CCl_3C\begin{matrix}\diagup\!\!\!\diagup O\\ \diagdown OH\end{matrix}$ when present in solution in alcohol or ether and the formula $CCl_3CO_2 : H$ when dissolved in water or petroleum ether. Other carboxylic acids are assumed to form equilibrium mixtures of these two modifications when dissolved in water or petroleum ether:

$$\underset{\text{Pseudo-acid}}{RC\begin{matrix}\diagup\!\!\!\diagup O\\ \diagdown OH\end{matrix}} \rightleftarrows \underset{\text{True acid}}{RC\left.\begin{matrix}\diagup O\\ \vdots\\ \diagdown O\end{matrix}\right\}\cdot H}$$

[1] M = metal.

The condition of equilibrium, as in the case of *keto-enol* modifications, depends upon the nature of the solvent, the nature of the substance, the character of R, etc. The isomerization of one modification into the other in solution may be explained as due to chemical causes as, for example, the formation of solvates or association products which possess different degrees of stability, viz.,



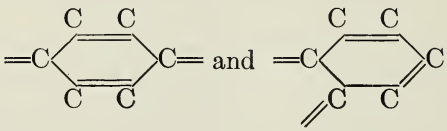
The influence of R is illustrated by the fact that the substitution of chlorine for hydrogen in acetic acid results in a condition of equilibrium which favors the formation of the true acid. The progressive changes in the condition of equilibrium which take place as a result of the introduction of one, two and finally three chlorine atoms, correspond to similar changes in absorption. Since, moreover, a fully ionized acid is optically identical with its salts the relative absorption of a given solution may be regarded as a direct measure of its condition of equilibrium. In the case of the fatty acids, however, because of their relatively weak absorption, optical methods are much less exact than determinations of electrical conductivity so that the latter are, therefore, generally preferred.

The relation between color and constitution was first developed by O. N. Witt [1] following the fundamental discovery of Graebe and Liebermann.[2] Witt's so-called "chromophore theory" attempted so to systematize the phenomena of color as to make it possible to synthesize a colored substance or a dye from its essential constituents. The appearance of color has for many years been connected with the introduction into an organic molecule of certain groups as for example NO_2,—N=N—, etc. When these groups are changed in any way, as in reduction to NH_2 and —NH—NH— respectively, the color which they imparted to a given substance disappears, but reappears again on oxidation of the so-called colorless "leuco-compound." Groups which like these by their mere presence seem to have the power to produce color are called *chromophore* groups, and the colored compounds which contain them are called *chromogens*. In order that a chromogen become a dye, and therefore capable of entering into direct or indirect relations with a fabric, it must possess in addition to a chromophore, a so-called *auxochrome* group.

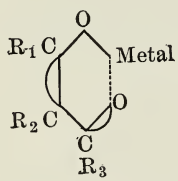
[1] Ber., **9**, 522 (1876); **21**, 325 (1888).
[2] Ber., **1**, 106 (1868).

The latter are characterized by the fact that they are capable of reacting with either acids or bases respectively to form salts. Examples of auxochromes are NH_2, OH, etc., and they not only enter into direct combination with fabrics such as silk or wool, but they also have the effect of deepening the color of the chromogen. To repeat, a chromogen is a substance which contains a chromophore group, while a dye, on the other hand, is a substance which contains both a chromophore and an auxochrome group. This in brief outlines Witt's original theory. It has been modified and very greatly extended in recent years and will now be considered in some of its ramifications and applications. The subject of chromophores and auxochromes, must, however, first be examined separately and in detail.[1]

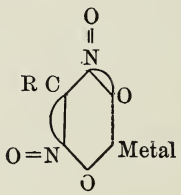
The most important chromophore groups are >C=O; > C=S; >C=N— (including azomethine); —N(O)—N— (azoxy); —NO· —NO_2; —N=N; and the quinoid groups[2]:



According to Werner's theory of partial valencies groups such as



Metal salts of 1–3 diketones



Dinitro-compounds

must also be regarded as chromophore groups, in which case the phenomenon of color is assumed to be due to the mutual saturation of partial valencies inside the molecule as represented by the dotted lines in the formulas. This particular phase of the subject cannot be discussed fully at this point but will be considered later in the chapter.

In general it may be said that chromophore groups contain the ele-

[1] J. Lifschitz, "Studien über die Chromophorfunktion," Zeitschr. wiss. Phot., **16**, 101, 140, 149, 269 (1916); **19**, 198 (1920); Ber., **50**, 897, 906 (1917); Zeitschr. physikal. Chemie, **95**, 1 (1920).

[2] Armstrong, Proc. Chem. Soc. **1892,** 101, 189, 195; **1893,** 53, 55, 63, 206; **1897,** 228; **1902,** 101; Jour. Chem. Soc. **87,** 1272, (1905).

ments, C, N, O, and S either in union with each other by double or triple bonds or present in so-called free organic radicals as single highly unsaturated atoms. Chromophore groups have been classified as either independent or auxiliary in character. For example, certain combinations such as NO and NO_2[1] have the power of forcing colored compounds even when in union with such groups as CH_3 and others which possess only very slight optical activity. The properties of these chromophores are the more marked [2] when they are compared with those of the second class. The latter are individually and singly incapable of producing color, but have the power of reinforcing each other and by a sort of cumulative action they are able to contribute to the generation of color. Thus, for example, the quinoid grouping which is so effective as a color bearer represents the combined action of four pairs of unsaturated atoms. In general it may be said that the great majority of colored substances owe their color not to the presence of one but of many chromophores.

J. Lifschitz [3] has recently classified chromophores according to conceptions embodied in Werner's theory. From this point of view they may be regarded as coordinately saturated or coordinately unsaturated. In the latter case three principal classes may be differentiated:

1. Monatomic chromophores (free radicals, dyes, additive compounds).

2. Diatomic chromophores. This class includes the great majority of the chromophores which have been mentioned above.

3. Chromophore systems of atoms. This class includes conjugated compounds and inner complex salts. Such systems are characterized in particular by the fact that they appear to act optically as separate units within the molecule.

In every case it must be remembered that the property of unsaturation represents only one of the several factors which operate in the formation of chromophores. According to H. Kauffmann [4] it is not even the controlling factor in determining color. For example it has not as yet been possible to demonstrate conclusively that depth of color bears a definite relation to the degree of unsaturation.[5] It is not even certain

[1] Compare H. Kauffmann, "Über den Zusammenhang zwischen Farbe und Konstitution bei chemischen Verbindungen"; Ahrens Sammlung chem. und chem.-techn. Vorträge, **9**; also "Die Valenztheorie," p. 432, Stuttgart, 1911 (Enke); Ber., **45**, 781, 2333 (1912); **46**, 3788, 3801, 3808 (1913); **49**, 1324 (1916); H. Ley, "Die Beziehungen zwischen Farbe und Konstitution bei organischen Verbindungen," p. 19, Leipzig, 1911 (Hirzel); R. Möhlau and R. Adam, Zeitschr. f. Farbenindustrie.

[2] Kauffmann, Ber., **40**, 2341 (1907).

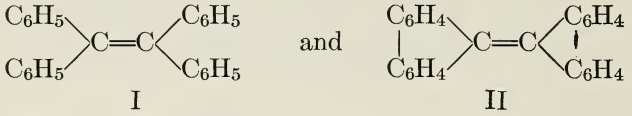
[3] Zeitschr. wiss., Phot., **16**, 107 (1916).

[4] Ber., **50**, 635 (1917).

[5] Lifschitz, Ber., **50**, 906 (1917); Ley, Ber., **50**, 243 (1917); **51**, 1808 (1918).

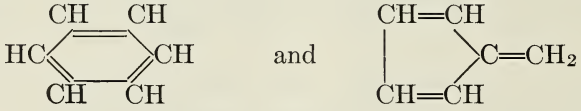
that the shifting of absorption in the direction of the red is exactly proportional to an increase in the unsaturated character of a compound.

The relative position of chromophores in the molecule is of great importance in the production of color. From the point of view of arrangement chromophores have been classified as *cyclostatic* and *streptostatic*, the former representing constituent parts of a cyclic and the latter being present in acyclic combinations. In general it may be said that density of atomic groupings, such as is associated with ring formation, tends to produce and also to strengthen color. Innumerable instances may be cited in illustration of this. In the case of the following compounds:



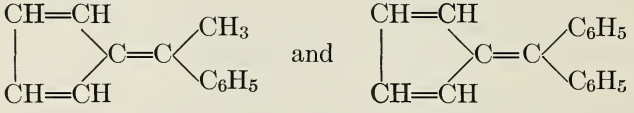
I and II

it has been observed, for example, that the first is colorless [1] while the second is red;[2] and in the case of the two isomers, benzene and fulvene,



one is colorless while the other is yellow. The difference in color in both instances is generally assumed to be due to a relatively greater density in the arrangement of the atoms in the colored compound.

The cumulative effect of chromophore groups in strengthening color is strikingly illustrated by a comparison of the derivatives of fulvene.[3] Thus, while fulvene itself is yellow, methyl phenyl fulvene possesses the color of a solution of chromic acid and diphenyl-fulvene is deep red: [4]



Carbonyl groups are much more effective chromophores than ethylene groups, since two such groups, when present in adjacent posi-

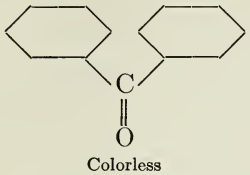
[1] Klinger and Lonnes, Ber., **29**, 2157 (1896).

[2] Graebe, Ber., **26**, 2354 (1893); **25**, 3146 (1892).

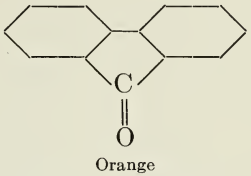
[3] Ber., **33**, 668, 851, 3395 (1900); **36**, 842 (1903); Annalen der Chemie, **319**, 226 (1901).

[4] Ber., **33**, 666 (1900); **37**, 2851 (1904); Annalen der Chemie, **349**, 333, 361 (1906); also Ley, Zeitschr. angew. Chemie, **1907**, 1305.

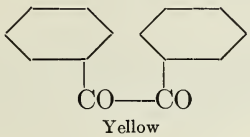
tions, possess the power of imparting color to the molecule containing them. For example, CH_3COCH_3 is colorless, $CH_3CO \cdot COCH_3$ is yellow, $CH_3CO \cdot CO \cdot COCH_3$ [1] is reddish orange, while $CH_3COCH_2COCH_3$ and $CH_3CO \cdot CH_2CH_2COCH_3$ are, on the other hand, colorless. The influence of density in atomic groupings is illustrated in the case of the following two pairs of substances:



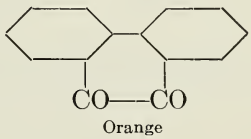
Colorless



Orange

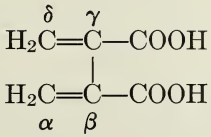


Yellow

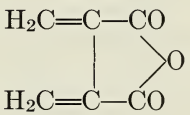


Orange

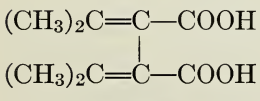
Numerous derivatives of butadiene β-λ-dicarboxylic acid and of its anhydride,



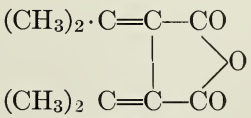
and



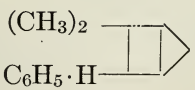
have been studied by H. Stobbe[2] and afford striking illustrations of the relation existing between color and constitution. Thus a comparison of the substances given in the following table shows that the aliphatic derivatives of these two substances are colorless, while both phenyl and furyl (C_4H_3O) derivatives are colored. This color deepens from yellow to orange to deep red steadily, as the number of such groups present in the molecule is increased:



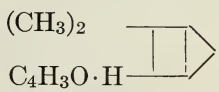
Colorless



Colorless



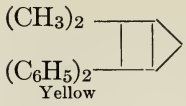
Light yellow



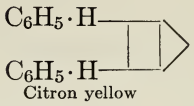
Orange

[1] Ber., **34**, 3047 (1901); **35**, 3309 (1902); **36**, 3221 (1903).

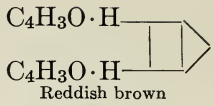
[2] Annalen der Chemie, **349**, 333 (1906); **380**, 1 (1911).



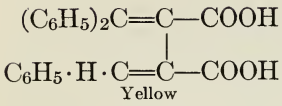
Yellow



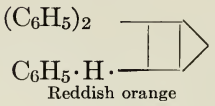
Citron yellow



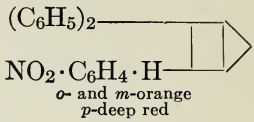
Reddish brown



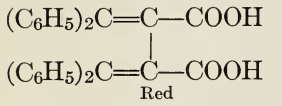
Yellow



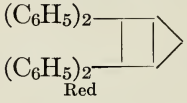
Reddish orange



o- and *m*-orange
p-deep red

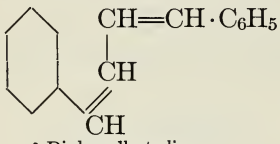


Red

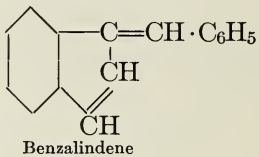


Red

As has been pointed out,[1] ring formation frequently brings about a deepening of color, as, to use another illustration, in the case of

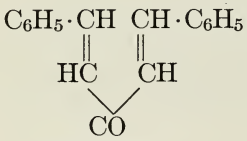


α- δ-Diphenylbutadiene
Colorless

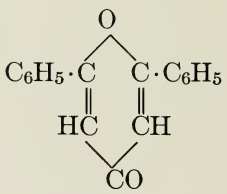


Benzalindene
Yellow

but this is not always the case. The closing of a straight chain of carbon atoms to form a heterocyclic ring which contains oxygen may, in fact, produce the opposite effect:



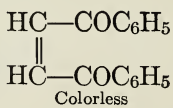
Dibenzalacetone
Yellow



Diphenylpyrone
Colorless

Differences in color have been observed to accompany differences in constitution in the case of a great many stereoisomers,—such as, for example, the two modifications of dibenzoylethylene discovered by C. Paal and Schulze.[2]

Yellow



Colorless

[1] Annalen der Chemie, **349**, 349 (1906).
[2] Ber., **33**, 3784 (1900); **35**, 168 (1902).

The stereoisomers of diethoxynaphthostilbene [1] and benzaldesoxybenzoin [2] represent other illustrations of phenomena of this class. To recapitulate, chromophores may be regarded as distinctly unsaturated groups. Two or more such groups are frequently necessary to produce color and in such cases density in arrangement tends to deepen or even in certain instances to generate color. H. Staudinger has recently pointed out as a result of his investigation of carbonyl groups,[3] that a direct relation exists between the degree of unsaturation of a substance and its color. Since conjugate systems of double bonds have been observed to be more unsaturated than two single pairs of unsaturated atoms, it should follow that such an arrangement is marked by a deepening of color. Staudinger maintains that this is in fact the case and that, moreover, the still less saturated systems of crossed double bonds show corresponding differences in color.[4] The relation between color and chemical reactivity is in every instance definitely marked, as may be seen by reference to the following table:

Quinones	very active,	colored
Unsaturated Ketones	↓ decreasing to	↓
Aldehydes		
Aromatic Ketones		
Acid derivatives	only slightly reactive,	colorless

The relation between absorption phenomena and a condition of unsaturation in organic compounds has been the subject of serious interest and speculation to many investigators. According to Kauffmann [5] the common cause of both manifestations is to be found in the shattering of the principal valencies of the atoms and their resolution into innumerable and scattered component forces (" Zersplitterung der Valenz.") To understand this conception it is necessary to develop Kauffmann's views in some detail.

It has been pointed out that color may be created and modified in an infinite variety of ways by the combination of chromophore groups. The mechanism of the process becomes clearer if the effect of introducing a new group into a chromogen of definite color is considered. In such a case the resulting change of color may be due either to the fact that the absorption bands have been shifted in the direction of the violet or the red, thus deepening or lightening the color, or it may be due to

[1] Jour. prakt. Chemie, **47**, 72 (1893).
[2] Ber., **34**, 3897 (1901); **45**, 76 (1912).
[3] Annalen der chemie, **384**, 45 (1911).
[4] Compare Friedlander, Ber., **47**, 1919 (1914); also Ber., **50**, 243, 630, 906 (1917).
[5] "Die Valenzlehre," p. 344 and following, Enke, Stuttgart, 1911.

the fact that the extinction in certain regions of the spectrum has been altered.

Characteristic changes in general properties and in color are caused by the action of auxochromes. As has already been stated such groups were first supposed to act exclusively as salt-forming groups, but recent investigations show that they possess other important properties. It has been demonstrated, for example, that OCH_3 and OC_2H_5 exercise an important function in the determination of color even though they are obviously not salt-forming groups. According to Kauffmann,[1] auxochromes may be broadly defined as groups of atoms which, while not possessing the properties of chromophores, are, nevertheless, able to strengthen the color of a chromogen. In cases where such groups possess in addition the power to form salts, their introduction into an organic molecule not only serves to modify the particular color of a given chromogen, but actually changes the chromogen into a dye.

The exact mechanism of the process by which changes in color are produced has been found to be much more complex than was at first supposed. In the case of derivatives of benzene, the color of a given chromogen has been found to be affected by the action of auxochromes only when the latter substitute in the ring.[2] Even under these circumstances the relative positions occupied by the different groups seem to constitute an important factor in the determination of color. Thus *o*-nitraniline is orange while *p*-nitraniline is yellow, or, in other words, the same groups may strengthen color in one position and not in another. The group NH_2 may be regarded as acting in the capacity of an auxochrome only when by direct substitution of the hydrogen in the ring it actually strengthens the color of the chromogen.

Having narrowed the process down to the substitution of ring hydrogen by specific groups in definite positions, the question as to the ultimate cause of the phenomena still remains unanswered. In general two opinions prevail. According to Kauffmann substitution brings about changes of a particular kind in the valency relationships of the carbon atoms of the ring. This conception does not find full expression in any of the structural formulas which are current at the present time, and is commonly referred to as the "auxochrome theory." In the opinion of still other chemists and theorists the changes which are brought about by the action of auxochromes, while due to differences in the distribution of affinity in the molecule, may be expressed in terms of structural formulas and therefore interpreted in terms of the "theory of molecular rearrangements."

[1] "Die Valenzlehre," p. 482.
[2] "Die Valenzlehre," p. 483.

Kauffmann's theory may now be considered in some detail. In general it may be said to be based upon certain observations in regard to the behavior of the vapor of aromatic compounds under the action of Tesla rays.[1] It has been observed that many substances in the gaseous state at great dilution and under low pressure absorb Tesla radiations and become luminous, emitting blue, violet, green, or yellow light. In the case of most substances this luminescence disappears at greater densities and higher pressures although there are certain notable exceptions to this general rule. For example, a few aliphatic compounds (especially ketones) and most aromatic compounds retain their luminescence at a relatively high pressure. These substances, according to Kauffmann, have certain characteristics in common. Thus, for example, derivatives of benzene which show a violet luminescence in Tesla radiations also dissolve in alcohol with a violet fluorescence. A comparative study of luminescing substances has led to the conclusion that the phenomenon is due to the specific arrangement of the atoms in the molecule, and, since a great many derivatives of benzene possess this property, the benzene nucleus has come to be regarded as a *luminophore.*

It has been observed further that the luminescence of different derivatives of benzene varies both as to color and intensity, and that although benzene itself is not luminous, it readily yields luminescent derivatives as a result of the substitution of such groups as NH_2, $NHCH_3$, $N(CH_3)_2$, OH, OCH_3, etc., in place of the hydrogen of the ring. In other words, those groups which have been most frequently observed to function as auxochrome groups, possess the power of strengthening luminescence and fluorescence in organic compounds. In order to explain simultaneous variations in these various properties among derivatives of benzene Kauffmann supposes that the ring itself changes as a result of substitutions, and that it is actually different in different substances. It is assumed that the energy of the molecule may be distributed in a variety of ways and that such variations correspond to differences in the chemical properties as well as in the physical properties of the substances. While an almost infinite number of arrangements is possible, certain ideal extreme conditions may be imagined to exist and these may be expressed in terms of constitutional formulas.

The first of these limiting ideal conditions is supposed to correspond roughly to Kekulé's formula for benzene and may be assumed to exist in all substances which possess fluorescent bands in the regions of the extreme ultra-violet, as for example benzene and its homologues. The second corresponds to the Dewar formula for benzene and may be

[1] Zeitschr. physikal. Chemie, **26**, 719 (1898); **27**, 519 (1898); **28**, 688 (1899); **50**, 350 (1905), etc.; also compare Ber., **33**, 1725 (1900); **34**, 682 (1901).

assumed to be present in all substances whose vapors emit a violet light under the influence of Tesla radiations. This condition is characterized by certain definite physical and chemical properties as, for example, anomalous magnetic rotation and to a lesser degree anomalous molecular refraction, accompanied by increased chemical reactivity, i.e., a tendency to oxidize readily, to form substitution products, to form quinoidal derivatives, etc. According to Kauffmann this condition, which is sometimes referred to as the " D " condition, finds its best expression in the quinoid formula:

These first two classes include all substances which give a violet fluorescence when dissolved in alcohol. A third condition of the benzene nucleus is characterized by the complete absence of luminescence and fluorescence and by decreased chemical reactivity. It results from the substitution of such groups as NO_2, CH_3CO, Br, etc.,[1] and was originally supposed to correspond roughly to the Claus formula for benzene. This assumption has not, however, been substantiated.

If three typical conditions such as have just been described actually exist, it follows that substitution in any given case must favor one at the expense of the others, and the particular effect of auxochromes must therefore be considered. The most important auxochromes are NH_2 and OH,[2] and of these the former is more powerful than the latter. Since both groups continue to function as auxochromes even after the hydrogen has been replaced,—as for example by methyl,—it follows that the characteristic properties of the auxochrome depend in each case upon the presence of the non-metallic element. In studying the effect of the substitution of hydrogen in the amino group it has been observed that methyl, as in $N(CH_3)_2$, strengthens the auxochromic properties of the radical, while negative groups, such as $COCH_3$, COC_6H_5, $=CH \cdot C_6H_5$, etc., when substituted for hydrogen as in $NHCOCH_3$, effectively weaken these properties. Salt formation completely neutralizes all power of NH_2 to function as an auxochrome group. The substitution of the hydrogen in hydroxyl, on the other hand, is accompanied in the case of methyl by a slight weakening and in the case of acetyl by a relatively great weakening of the auxochromic properties of

[1] "Die Valenzlehre," p. 500.

[2] Compare E. Noelting, Chem. Zeitung, **1910**, 1016.

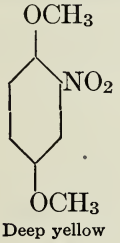
the radical. Salt formation in this case has the effect of greatly increasing the power of the group. Thus ONa is almost as strong an auxochrome as NH_2.

The following series of auxochromes has been arranged by Kauffmann in the ratio of their respective opto-magnetic anomalies:

$OCOCH_3$	OCH_3	$NHCOCH_3$	NH_2	$N(CH_3)_2$	$N(C_2H_5)_2$
—0.26	+1.457	+1.949	+3.821	+8.587	+8.816

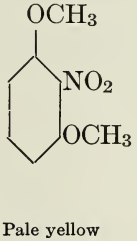
The figures represent the relative displacement of absorption due to the substitution of the various groups and are, therefore, a measure of the relative activity of each radical. It should be noted that an acetylated hydroxyl group does not function as an auxochrome, while methoxyl and acetylamino groups are very weak auxochromes.

Two methoxyl groups in the *para*-position mutually reinforce each other, and have a combined value of +2.999. In general when two or more auxochromes are present in a molecule, their effect upon color seems to depend to a very great degree upon their relative positions, as is strikingly illustrated in the case of the dimethoxynitro-benzenes:



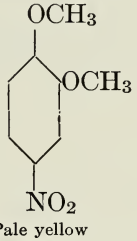
Deep yellow

I



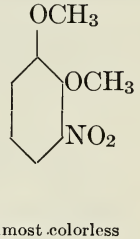
Pale yellow

II



Pale yellow

III



Almost colorless

IV

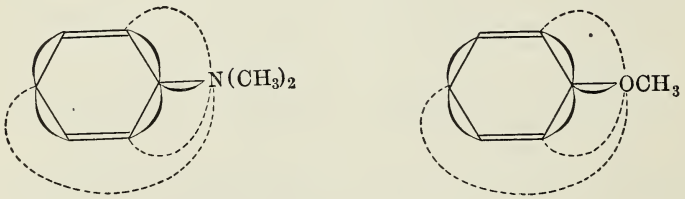
Condensed ring systems such as naphthalene and anthracene have the same effect as auxochrome groups and produce a shifting of the absorption bands of benzene in the direction of the visible spectrum.

It must be clearly recognized that, according to the conceptions of the auxochrome theory,[1] the change in color which accompanies substitutions is due on last analysis not solely to the auxochrome but also to the changed character of the chromogen itself. The substitution of auxochrome groups is undoubtedly very far reaching and affects not only the absorption, but also the refraction and the magnetic rotation of the substance. Luminescence is also affected, as has already been pointed out. Such changes and others have a common basis, according to Kauffmann, in the fact that substitution always involves fundamental readjustments in the distribution of energy in the case of both

[1] Ber., **39**, 1959 (1906).

the auxochrome and of the chromogen. In particular it is assumed that in this process the unit valencies of the atoms present in both groups are very much broken up. The systematic development of this idea follows.

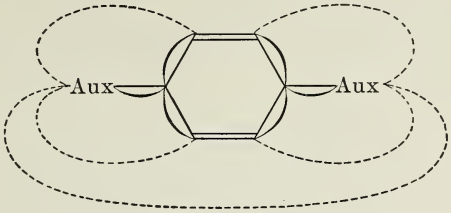
The fact that an auxochrome such as $N(CH_3)_2$ loses its power when nitrogen passes from the trivalent to the pentavalent condition, can be explained only by supposing that this power depends in some way upon the presence of two potentially free valencies. It is, therefore, reasonable to assume that, when an auxochrome such as $N(CH_3)_2$ substitutes for hydrogen in the benzene nucleus, this process involves an exchange of affinity not only between nitrogen and the carbon atom with which it is in direct union, but also between it and the other five carbon atoms of the ring, with the result that nitrogen actually passes into what approximates the pentavalent condition. Reasoning by analogy auxochromes which contain oxygen function as such because of the tendency of oxygen to pass into the quadrivalent condition. Moreover, since this tendency to exercise its higher valencies is less marked in the case of oxygen than in the case of nitrogen it is easy to understand why the former element is a less effective auxochrome than the latter. The distribution of the two higher valencies in the case of both elements is represented as taking place according to the following scheme:



It should be noted that this exercise of affinity involves the carbon atoms in the *ortho-* and *para-* but not in the *meta-*positions to the substituting group.

This exchange of valency cannot be conceived in terms of a single line joining the central atom of the auxochrome with the adjacent carbon atom of the ring, but must rather be imagined as due to the saturation of innumerable lines of force which radiate in all directions from the oxygen or nitrogen atom respectively. According to this conception the *ortho-* and *para-*positions in the benzene ring may be regarded as centers toward which an unusually large number of lines of force converge and they should, therefore, be centers of great chemical activity. If follows, also that the quinoidal arrangement of the carbon atoms in the ring,

which has already been referred to as the condition D, is favored by the substitution of strong auxochromes in the *para*-position to each other. This becomes apparent by reference to the following diagram:



It is significant in this connection that the presence of even weak auxochromes in the *para*-positions imparts the property of luminescence to aromatic compounds. Indeed the strongest luminophores contain *para*-auxochromes. So important are these particular positions in the determination of the specific properties of a given substance that their mutual reinforcement is referred to by Kauffmann as the "law of distribution of auxochromes."[1]

According to this conception the saturation of the affinity of a substituting group is not concentrated at a given point in the benzene molecule but must be imagined as distributed over the whole radical. Under such circumstances two groups in either the *ortho*- or *para*-positions with reference to each other interfere with each other, so that the full exchange of affinity between either auxochrome and the benzene radical becomes impossible. It is, therefore, easy to understand why substitution in these positions produces what may be termed decentralization of valency. Many instances of the decentralization of chemical functions have been noted.[2] It has been observed, for example, that while a substance such as acetone which contains only one carbonyl group absorbs in the region of the ultra-violet and is, therefore, colorless, substances which possess two or more such groups in adjacent positions exhibit the phenomenon of color:

$CH_3 \cdot CO \cdot CO \cdot CH_3$	$CH_3 \cdot CO \cdot CO \cdot CO \cdot CH_3$
Yellow.	Orange.

This is explained by supposing that the introduction of a second and of a third carbonyl group in positions adjacent to the first produces an increase in the decentralization of the chromophore function and that this is accompanied by corresponding changes in the optical properties

[1] Ber., **39**, 2724 (1906); also "Die Valenzlehre," p. 503; compare Ber., **46**, 3792 (1913); and **47**, 1919 (1914).

[2] Ber., **47**, 1324 (1916); also "Die Naturwissenschaften," **5**, 21 (1917).

of the substance. The relationship which is expressed by means of conjugate systems of double bonds seem to be definitely responsible for the phenomenon, since the presence of two isolated carbonyl groups in a molecule is not productive of color. This is strikingly shown by a comparison with the following substances:

$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$ Colorless. $\qquad$ $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$ Colorless.

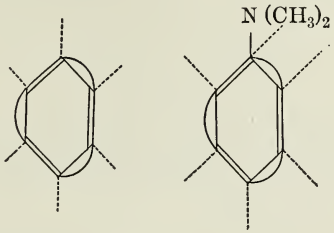
Kauffmann [1] recently discovered that the relative acidity or basicity of certain compounds is a direct measure of the degree to which any of the principal valencies have been broken up into smaller units of affinity. This observation proved to be so general in its nature that Kauffmann formulated it as the "law of the decentralization of chemical functions," according to which an increase in the acid and basic properties of a compound is assumed to accompany any increase in the decentralization of chemical affinity.[2]

Kauffmann supposes that while the molecule of a given compound necessarily possesses a fixed and definite structure it may, nevertheless, exist in an almost endless variety of phases which depend in large measure upon external conditions such as heat, etc. For example, if z represents the fraction of affinity by which any two atoms are bound together in a given molecule, it follows according to Kauffmann's conception that this value is constant only under perfectly definite conditions and that it varies continuously with slight changes in conditions. This is known as the "principle of shifting conditions" according to which the various forms of union between the atoms of a given molecule are supposed to vary greatly in value, depending upon conditions, and not to represent fixed and definite units of affinity.[3] The most reactive positions in the molecule are, moreover, those which are characterized by the greatest fluctuations in the value of the strength of union between any two of its atoms (z). Further applications of the law of the decentralization of chemical affinity will be referred to again later.[4]

H. Staudinger and N. Kon in their paper on "The Reactivity of Carbonyl")[5] differ from Kauffmann in their interpretation of the relation of color to constitution. They explain the fact that auxochromes increase the reactivity of carbonyl and other unsaturated groups by supposing that the presence of auxochromes increases the partial valencies on these groups. Since, however, no deepening in the color of

[1] Ber., **46**, 3801 (1913); **52**, 1425 (1919).
[2] Ber., **53**, 263 (1920).
[3] Ber., **49**, 1324 (1916); **52**, 1425 (1919).
[4] Ber., **47**, 1324 (1916); **52**, 1422 (1919).
[5] Annalen der Chemie, **394**, 45 (1911).

a substance is observed unless the auxochrome is bound to the carbonyl or other chromophore by means of the benzene ring, it is necessary to make an additional assumption and to suppose that under the influence of the auxochrome the normally neutral ethylene bonds of the ring become actively unsaturated. In other words, the partial valencies on the carbon atoms in the ring are simultaneously increased:



Speculation along these lines was stimulated in 1878 by the discovery that fuchsine and related dyes may be regarded as derivatives of triphenylmethane.[1] A detailed study of these substances by E. and O. Fischer demonstrated that dyes are not formed immediately as the result of introducing hydroxyl and amino groups into the triphenylmethane molecule, since derivatives such as $CH(C_6H_4NH_2)_3$, for example, are colorless even in the form of their salts. They readily oxidize, however, to give true color bases, as for example $COH(C_6H_4NH_2)_3$, and the latter react with acids to give salts which dissolve in water without hydrolysis.

In studying the action of acids upon derivatives of triphenylcarbinol it has been observed that salt formation is always accompanied by the loss of one molecule of water and cannot, therefore, be regarded as a process involving simply the addition of one molecule of acid to an amido group.

$$\underset{\text{Pararosaniline}}{C_{19}H_{19}N_3O}+HCl \rightarrow H_2O+\underset{\text{Parafuchsine}}{C_{19}H_{18}N_3Cl}$$

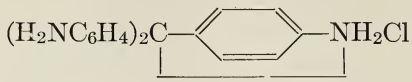
Various interpretations of this reaction have been suggested. E. and O. Fischer assume that it takes place in two stages:[2]

$$(H_2NC_6H_4)_2C\begin{cases}C_6H_4NH_2\\OH\end{cases}+HCl=(H_2NC_6H_4)_2C\begin{cases}C_6H_4NH_2\cdot HCl\\OH\end{cases}$$

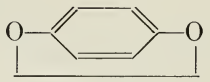
$$(H_2NC_6H_4)_2C\begin{cases}C_6H_4NH_2\cdot\overline{|H|}Cl\\\underline{|OH|}\end{cases}=H_2O+(H_2NC_6H_4)_2C\underline{C_6H_4NH_2Cl}$$

[1] Annalen der Chemie, **194**, 286 (1878); also Ber., **37**, 3355 (1904).
[2] Ber., **12**, 2348 (1879).

This conception supposes a complete change [1] in the condition of one benzene nucleus since



is evidently directly analogous to the peroxide formula of quinone.

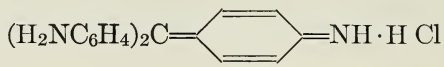


Another explanation was advanced by Rosenstiehl,[2] who assumed that the acid reacted directly with hydroxyl and that the amido group was in no-wise involved in the reaction:

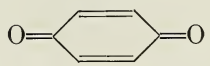
$$\underset{\text{Pararosaniline}}{(H_2NC_6H_4)_3C\cdot OH} + HCl = H_2O + \underset{\text{Parafuchsine}}{(H_2NC_6H_4)_3CCl}$$

This latter interpretation is supported by the fact that dyes of this type are capable of reacting with three additional molecules of hydrochloric acid to form salts, and also by the fact that parafuchsine may be formed directly from carbon tetrachloride and aniline. It was not, however, generally accepted at that time, largely because it failed to account for the obvious analogy existing between pararosaniline and hydrocyan pararosaniline.[3]

Although Fischer's formula for parafuchsine was undoubtedly quinoidal in character, the full significance of this was not realized until 1888, when R. Nietzki introduced it into his text-book in somewhat modified form, viz.,



This formula was preferred to Fischer's original formula because it was closely analogous to Fittig's formula for quinone,



which was then in current use, although there seemed to Nietzki to be no very fundamental difference between the two.[4] Thus, in terms of the

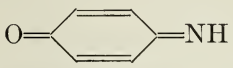
[1] Ber., **26**, 2223 (1893).

[2] Bull. soc. Chimie (2), **33**, 342 (1880); Compt. rend., **116**, 194 (1893); **120**, 192, 264, 331, 740 (1895).

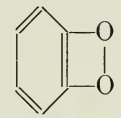
[3] Compare Fischer and Jennings, Ber., **26**, 2222 (1893).

[4] "Chemie der Organischen Farbstoffe," R. Nietzki, 1901, p. 120.

Fischer-Nietzki formula fuchsine and other substances of this class may be regarded as derivatives of quinonimide:

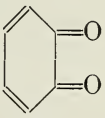


This conception has been further developed and somewhat modified recently as the result of the discovery of two isomeric *ortho*-quinones. R. Willstätter [1] observed that when pyrocatechol is carefully oxidized by means of silver oxide in the absence of moisture, a colorless oxidation product is formed. This substance is very unstable and isomerizes quickly to give a red compound. Both of these products possess all of the characteristic properties of quinone, and seem therefore to correspond respectively to the formulas:



Colorless

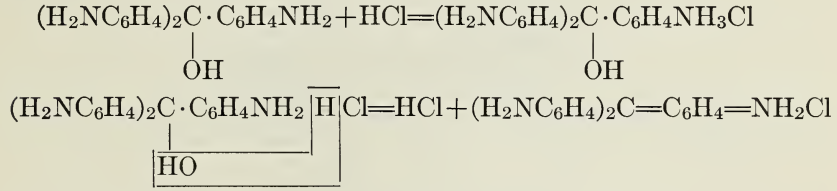
and



Red

Isomerism of this sort is, of course, also possible in the case of the *para*-quinones, although as yet no colorless compound corresponding to the peroxide formula has been isolated.

According to this interpretation it is necessary to assume that the color bases possess a very different structure from the dyes themselves, and that the transformation from pararosaniline into parafuchsine, for example, takes place in the following manner:

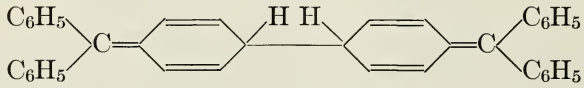


To explain the formation of salts containing three additional molecules of acid it is supposed that two molecules of acid combine with the two remaining nitrogen atoms, and that the third combines with the quinone nucleus as a whole. This latter reaction is conceivable, since it is known that quinone itself possesses the characteristic property of adding one molecule of hydrochloric acid. Similar interpretations apply to a large number of phenomena. Indeed the Fischer-Nietzki formula was found to offer a satisfactory explanation in so many cases that it came to to be very generally accepted, and further discussion of the problem gradually ceased.

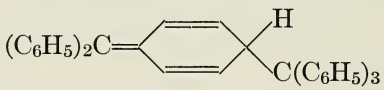
[1] Ber., **41**, 2580 (1908); **44**, 2171 (1911).

In 1900 the structure of dyes of the triphenylmethane type again became the subject of controversy as the result of Gomberg's discovery of the so-called triphenylmethyl. This discovery led to the revision of certain fundamental conceptions regarding both the physical and chemical properties of the element carbon and most therefore be considered in some detail.

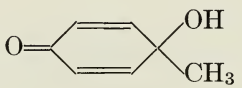
The discovery of the triphenylmethyl radical has been referred to earlier in this text and the fact has been noted that although concentrated solutions of hexaphenylethane are colorless, these solutions become yellow on dilution. The application of the chromophore theory in the interpretation of this phenomenon is obviously difficult, if, as has been assumed, the color is due to the formation of the free triphenylmethyl radical $(C_6H_5)_3C$..... The first theory to account for color was advanced by Heintschel [1] and was based upon the assumption that the substance is bimolecular:



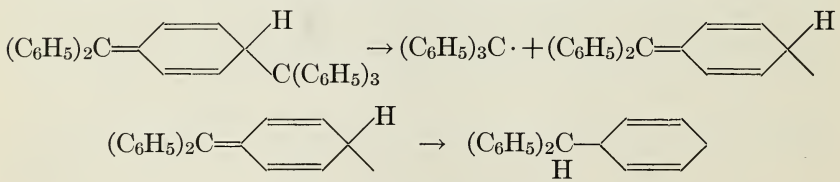
But while a quinoidal configuration served to account for the instability and also for the color of the substance, it failed to explain certain other properties as, for example, the tendency of the substance to form peroxides and other addition products. This explanation was therefore soon abandoned in favor of another which was advanced by P. Jacobson [2] and which assumed the following configuration of hexaphenylethane:



According to this formula the substance may be regarded as a derivative of quinol:

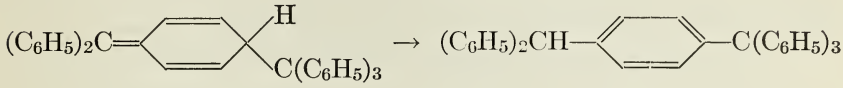


and might, therefore, be expected to undergo rearrangement in the sense



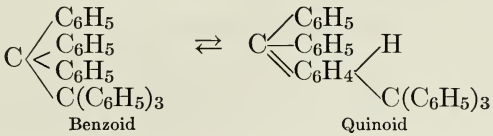
[1] Ber., **36**, 320 (1903).
[2] Ber., **38**, 196 (1905).

since in quinol both the hydroxyl and methyl groups are mobile and readily migrate into the ring. This formula affords a satisfactory explanation for the color and instability of the substance and also serves to account for such rearrangements as are, for example, represented in the formation of benzhydrol tetraphenylmethane:



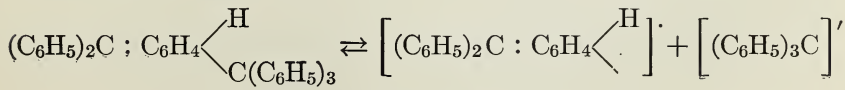
It presupposes a bimolecular formula and is thus in agreement with the earlier molecular weight determinations. Further, by assuming the possibility of rearrangements which involve the formation of the radical $(C_6H_5)_3C$, it explains why the substance reacts as if it were itself triphenylmethyl. This very ingenious formulation of the constitution of hexaphenylethane was, however, abandoned in turn and a third theory was advanced to take its place. The latter, which is current at the present time, resulted from a very exact investigation of the behavior of solutions of hexaphenylethane, but in order to understand the facts upon which it is based it is now necessary to review certain of the properties of this very interesting substance.

It has been stated that triphenylmethyl is a colorless crystalline solid which dissolves in various solvents to give yellow solutions. Gomberg [1] attempted to explain this phenomenon by supposing that the substance is capable of existing in the form of two isomeric modifications:



Benzoid I ⇄ Quinoid II

Of these the first is colorless and on solution passes into the second which is yellow. The yellow modification on evaporation of the solvent rearranges to give a colorless compound. In order to explain the great reactivity of solutions containing triphenylmethyl, Gomberg made the further assumption that the substance in solution dissociates into a benzoid and a quinoid ion:



[1] Compare Schmidlin, Ber., 41, 2471 (1908).

By assuming that benzoid ions are stable in certain solutions, and that under such conditions the quinoid modification undergoes immediate isomerization into the more stable form, it is possible to account for the great reactivity of the given solutions, since the benzoid ion is itself nothing more or less than triphenylmethyl.

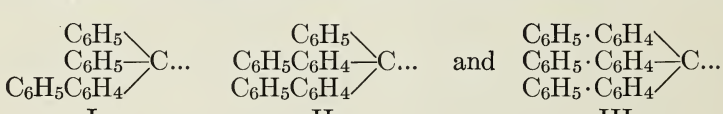
The collective reactions of triphenylmethyl may be accounted for on the basis of the following closely related hypotheses:

1. Tautomerism in the sense of I $\rightleftarrows$ II as shown above.

2. The partial dissociation of II in all solvents to form quinoid and benzoid ions.

3. Tautomerism in the sense of benzoid ions $\rightleftarrows$ quinoid ions.[1]

It has, however, already been pointed out in the chapter on free radicals, where the investigations of W. Schlenk and others were fully reviewed, that the relations which have just been described are much more simple in character than the present discussion might lead one to suppose. It may be remembered that Schlenk succeeded in preparing the following triaryl derivatives of triphenylmethyl, and that while I



and II closely resemble triphenylmethyl in being colorless and bimolecular in the solid state, III is deep violet in color, monomolecular in the solid state, and is in general an exceedingly unstable substance. These derivatives of triphenylmethyl dissolve in various solvents to give solutions which are respectively orange and deep red in color the intensity of color deepening as we approach III. As in the case of triphenylmethyl, molecular weight determinations show that such solutions contain equilibrium mixtures of mono- and bi-molecular modifications:

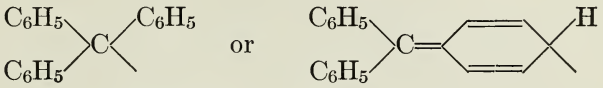
$$Ar_3C\cdot CAr_3 \rightleftarrows 2Ar_3C...$$

and that the intensity of color due to dilution corresponds to the degree of dissociation of the bimolecular into the monomolecular form. The reverse reaction corresponds, as J. Piccard has demonstrated, to diminution of color and a simultaneous increase in the values representing the molecular weights until finally in concentrated solutions the color almost disappears and the molecular weights approximate those of the respective hexaphenylethanes.

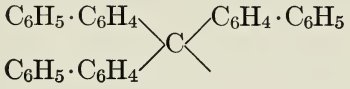
These observations lead definitely to the important conclusion that the appearance of color is directly associated with the existence of a free

[1] Ber., **40**, 1883 (1907)

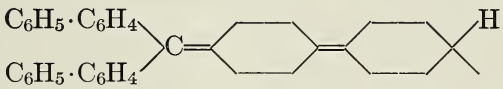
triaryl radical and that it therefore depends upon the unsaturated condition of the methane carbon atom or, in other words, to the presence of free valency. This interpretation has had an important influence upon the development of the theory of the relation between color and constitution, but, before this matter can be considered in detail, it will be necessary to review some of the earlier discussions in regard to the possible configuration of colored triarylmethyl radicals. Two possible configurations have been suggested, namely:



and



or



The relative merits of these formulas depend upon certain considerations which may now be briefly reviewed.

Following closely upon the discovery of triphenylmethyl Norris and Sanders [1] and also Kehrmann and Wentzel [2] observed that the colorless triphenylmethyl chloride and triphenyl carbinol dissolve in concentrated sulphuric acid to give yellow solutions. Parafuchsine behaves in the same way and in both cases the solution loses its yellow color on dilution, and a colorless carbinol is precipitated. These reactions are difficult to explain. In general they resemble the decomposition of salts of hydrochloric acid by the action of H_2SO_4, and if this analogy holds the triphenylmethyl radical must be assumed to possess basic properties:

$$(C_6H_5)_3CCl + HOSO_2OH = HCl + (C_6H_5)_3C \cdot OSO_2OH$$

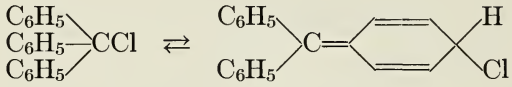
This does not, however, account for the color of the resulting solution since it does not presuppose the formation of a chromophore, and if $(C_6H_5)_3C \cdot Cl$ is colorless, a sulphate similarly constituted must also be assumed to be colorless.

Kehrmann and Wentzel then discovered that triphenylmethyl chloride exists in two modifications one, of which is white and the other orange yellow, the latter being formed when triphenyl carbinol is dis-

[1] Am. Chem. Jour, **25**, 54 (1901).
[2] Ber., **34**, 3815 (1901).

solved in acetic acid and then treated with concentrated hydrochloric acid. The resulting yellow solution was found to be stable for hours if allowed to stand, but lost its color on the addition of water. The colorless chloride was also found to dissolve in liquid sulphur dioxide with a bright yellow color. Triphenylmethyl also forms a colored perchlorate, $(C_6H_5)_3C \cdot ClO_4$, which has been isolated, as well as a series of colored double salts, as for example $(C_6H_5)_3C \cdot Cl \cdot AlCl_3$; $(C_6H_5)_3C \cdot Cl \cdot SnCl_4$.

Kehrmann and Wentzel interpret these phenomena by supposing that triphenylmethyl chloride and similar substances exist in two tautomeric modifications, one of which is colorless, ether-like, and benzoid in character, while the other is yellow, salt-like, and semi-quinoid or quinolic in character:

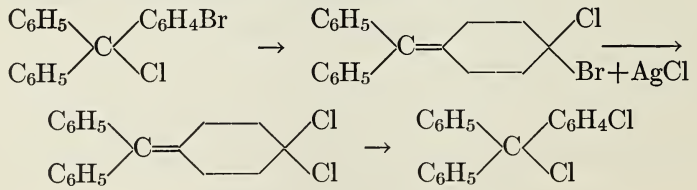


The essentially salt-like properties of the yellow modification have received confirmation as the result of a series of investigations undertaken by Gomberg and Cone.[1] They observed for example that when tribromtriphenylmethyl chloride, $(BrC_6H_4)_3C \cdot Cl$, was dissolved in liquid sulphur dioxide, the solution on evaporation gave monochlordibromtriphenylmethyl bromide. This product is essentially different from the original substance in that it reacts readily with silver chloride:

$$\begin{matrix}(BrC_6H_4)_2\\ ClC_6H_4\end{matrix}CBr + AgCl = AgBr + \begin{matrix}(BrC_6H_4)_2\\ ClC_6H_4\end{matrix}CCl$$

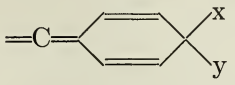
Thus while tribromtriphenylmethyl chloride contains three bromine atoms all of which are in union with ring carbon and therefore relatively inactive, its isomer contains one bromine atom which is in union with methane carbon and is, therefore, readily displaceable.

Monobromtriphenylmethyl chloride behaves similarly when dissolved in sulphur dioxide. In this case Gomberg and Cone interpret the reaction as taking place in the following way:



[1] Annalen der Chemie, **376**, 183 (1910).

Doubt has been expressed as to the value of this interpretation. It offers, for example, no satisfactory explanation for the phenomenon of color since, substances of the general formula



must be regarded as derivatives of quinol and are not in any sense true quinone derivatives. Baeyer and Villiger [1] point out, moreover, that if true quinones are actually present in solutions of triphenylmethyl chloride in concentrated sulphuric acid, and in solutions of its colored double salts, the existence of these substances should manifest itself in the increased sensitiveness of such solutions to the action of oxidizing and reducing agents, etc. Such is not, however, the case.

Baeyer and Villiger [2] therefore advanced the theory that in all such cases color could be explained as due to salt formation:

$$\underset{\text{Colorless}}{(C_6H_5)_3COH} + HOSO_3H(HCl, \text{ etc.}) \rightarrow H_2O + \underset{\text{Yellow}}{(C_6H_5)_3C \cdot OSO_3H}(Cl, \text{ etc.})$$

They had discovered, as a result of earlier investigations, that tertiary alcohols possess basic properties [3] and they, therefore, concluded that salt formation was directly analogous to the action which takes place between inorganic acids and bases, as for example KOH and HCl. At first sight this explanation seems to be the same as that which Rosenstiehl advanced in 1888 to explain the formation of fuchsine, but it differs in one important respect. Baeyer and Villiger conceived that the carbon atom which is present in the triarylmethyl radical functions in exactly the same way as the nitrogen atom in the ammonium radical, and that the complex $(C_6H_5)_3C$ therefore plays the part of a metal in the resulting salt. They assume, moreover, that this change in function is accompanied by a change in the character of one of the valencies of the carbon atom, and in order to distinguish between the ordinary non-ionizable valencies of carbon and such a metallic ionizable valence, they represent the latter by means of a waving line ~~~~~ and refer to it as a carbonium valence.

Both triphenyl carbinol and triphenylmethyl chloride may be regarded as possessing the usual formulas

$$(C_6H_5)_3COH \quad \text{and} \quad (C_5H_5)_3CCl$$

[1] Ber., **35**, 1195 (1902).

[2] Baeyer, Villiger, and others on the Carbonium Theory: Ber., **35**, 1754, 3013 (1902); **36**, 2774 (1903); **37**, 597, 1183, 2848, 3191 (1904); **38**, 569, 1156 (1905); **40**, 3083 (1907); **42**, 2624 (1909).

[3] Ber., **35**, 3015 (1902).

when present in the solid state since their basic properties are not apparent in this form. The basic functions of these substances become evident, however, when they are dissolved in the presence of certain metallic chlorides, concentrated sulphuric acid, etc., and under such conditions they may be formulated respectively as:

$$(C_6H_5)_3CCl + SnCl_4 = (C_6H_5)_3C{\sim}Cl \cdot SnCl_4$$

$$(C_6H_5)_3C \cdot OH + H_2SO_4 = H_2O + (C_6H_5)_3C{\sim}OSO_3H$$

Salts of methoxy and halogen derivatives of triphenyl carbinol may be formulated in an analogous way.

The phenomenon itself is referred to as *halochromism*,[1] and is defined by Baeyer as the transformation of a colorless or weakly colored substance into an intensely colored salt without the simultaneous formation of a chromophore group, such as, for example, the quinoid group.

In order to verify this theory it was necessary to demonstrate that alcohols such as triphenyl carbinol actually possess basic properties and that they combine with acids to give true salts. With this end in view Baeyer and Villiger endeavored to increase the basicity of substances of this type by substitutions of hydrogen in the benzene ring. They, therefore, prepared the *ortho-*, *meta-*, and *para*-trianisyl carbinols and found that all of these compounds possess greater basicity than the corresponding triphenyl carbinols, as is evident from the fact that they react even with dilute acids to form well-defined salts. Substitution in the *para* position was observed to produce the greatest relative increase in basic properties while that in the *meta* position produced the least.

The chloride $(CH_3OC_6H_4)_3C \cdot Cl$ is colorless, but combines with an excess of hydrochloric acid to form a red salt. A nitrate having the composition $(CH_3O \cdot C_6H_4)_3C \cdot ONO_2 + 1\frac{1}{2}HNO_3$ is also intensely colored.[2]

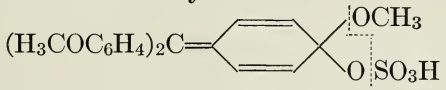
The essentially salt-like character of substances of this type has been demonstrated by P. Walden, who discovered that triphenylchlormethane and triphenylbrommethane dissolve in liquid sulphur dioxide to give solutions which are yellow in color and which resemble electrolytically dissociated salts in the way in which they conduct the electric current. Schlenk and Marcus[3] were subsequently able to show that the sodium salt of triphenymethyl actually suffers electrolytic dissociation during the passage of the electric current

$$(C_6H_5)_3C \cdot Na \rightarrow [(C_6H_5)_3C]^- + Na^+$$

[1] Ber., **51**, 1828 (1918).
[2] Ber., **35**, 1200 (1902).
[3] Ber., **47**, 1678 (1914).

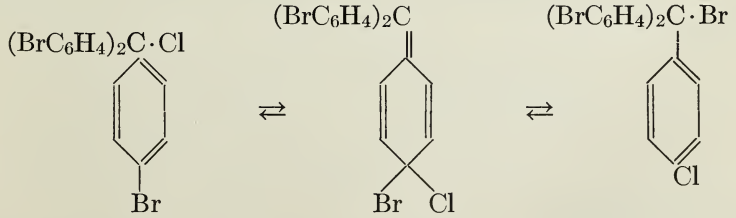
and that free triphenylmethyl is deposited in considerable quantities at the anode following the neutralization of the electric charge of the dissolved ion.

But even if triphenyl carbinol and its derivatives may be assumed to be true bases which form salts in the normal way with acids, the final constitution of these substances still remains to be determined. It will be recalled that the Kehrmann-Gomberg formula assumes a quinoidal configuration for the molecule. If, however, the sulphate of trianisyl carbinol is formulated in this way



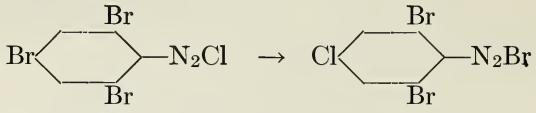
it should follow that methyl sulphuric could be readily split off in the sense indicated by the dotted lines; but as a matter of fact this is not the case. Baeyer and Villiger have pointed out other facts which are in direct contradiction to the Kehrmann-Gomberg formula. For example during the process of introducing successively one, two, and three methoxy groups into the molecule of triphenyl carbinol, they discovered that the increase in basicity is not an additive function of the molecule but that it takes place according to the law of geometrical progression. Thus if 1 equals the basicity of triphenyl carbinol, $1+n$ will equal the basicity of monomethoxytriphenyl carbinol, $(1+n)^2$ that of dimethoxytriphenyl carbinol and $(1+n)^3$ that of trimethoxytriphenyl carbinol. From this it follows that the three aryl groups function in exactly the same manner. Such a relation would be obviously impossible if one of these groups were quinoid while the other two were benzoid in structure.

The strongest evidence in support of the Kehrmann-Gomberg hypothesis is offered by the fact that tribromtriphenylmethyl chloride on solution in liquid SO_2 and evaporation of the solvent gives an isomeric substance containing a reactive bromine atom. This transformation has already been referred to and has been interpreted in the following manner:



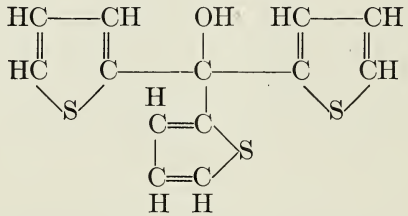
This explanation of the phenomenon is, however, opposed by Schlenk and Marcus who hold that the assumption of such a fundamental trans-

formation in the structure of the molecule is not justified by the facts of the case. An increase in the chemical reactivity of one bromine atom as a result of the change, by no means necessitates the assumption of quinoid structure, since similar phenomena have been observed in cases where no color changes have been involved. For example, tribrombenzene diazonium chloride readily rearranges into dibrommonochlorbenzene diazonium bromide.



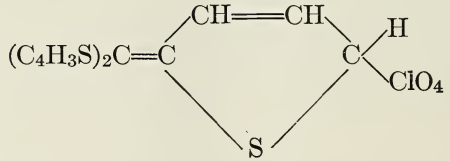
when dissolved in alcohol in the cold or even in the solid state upon standing, and this transformation takes place without any apparent change in color during the process.[1]

Certain instances of changes in color due to salt formation, and similar in character to those which have been described in the case of the triarylcarbinols, have been observed in cases where any explanation of the phenomenon on the basis of a quinoid structure is difficult. For example, A. Tschitschibabin and Gawrilow,[2] on the one hand, and W. Schlenk and R. Ochs[3] on the other, have succeeded in preparing trithienyl carbinol.



and have found that this substance dissolves in acids to give orange-brown solutions. According to Schlenk and Ochs the perchlorate resembles triphenylmethyl perchlorate in a most amazing manner.

Although it at first seemed impossible to explain the facts by supposing a quinoid rearrangement, the following formula for trithienylcarbinol:



[1] Ber., **30**, 2334 (1897).

[2] Jour. Russ. Physikal. Chem. Ges., **46**, 1614 (1914); Chem. Centralbl., **1915**, II, 78.

[3] Ber., **48**, 676 (1915).

was, nevertheless, finally constructed. This interpretation of the phenomenon was due in part to the discovery of the quinoid character of maleic anhydride and its derivatives by P. Pfeiffer and T. Bottler.[1]

Hantzsch has, moreover, recently pointed out on the basis of optical investigations that it is by no means necessary to abandon entirely quinoid formulas for the triphenylmethane dyes, since many of the properties of these substances may be satisfactorily accounted for by assuming that they represent conjugated quinoid combinations.[2] If the absorption curves of triphenyl carbinol, and hexamethyltriaminotriphenyl carbinol are compared (Fig. 1), it is apparent that the latter (curve 2) possesses a stronger absorption than the first (curve 1), but that both represent relatively simple types of color-bases. The trans-

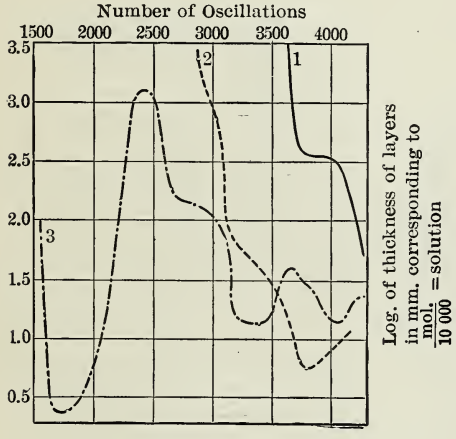


Fig. 1.

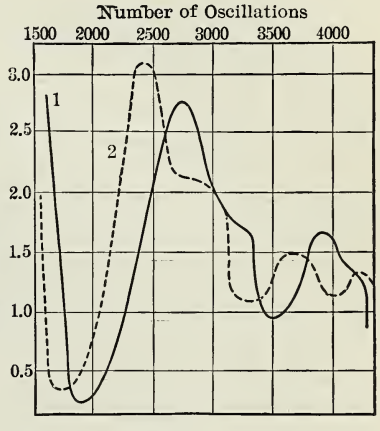


Fig. 2.

formation from hexamethyltriaminotriphenyl carbinol into its salt (crystal violet) is, on the other hand, accompanied by marked changes in optical properties, since the latter substance is characterized by banded absorption extending into the region of the visible spectrum (curve 3). Many other instances might be cited to show that as a rule free color bases possess relatively simple absorptions and that banded absorption arises as the direct result of salt formation. It is rather remarkable to find in this connection that two dyes which appear to the eye to be so distinctly different as crystal violet and fuchsine, should possess absorption curves which vary so little as those which are represented in Fig. 2.

Indifferent solvents seem to have very little effect upon the absorption of dyes as is apparent from a study of the absorption curves of crystal violet in solution in chloroform, alcohol, and water respectively (Fig. 3).

[1] Ber., **51**, 1828 (1918). [2] Ber., **52**, 509 (1919).

The flattening of the curve in the case of the aqueous solution may be accounted for on the assumption that an unstable addition product is formed by the action of the solvent upon the quinoid-cation of the dye.

In comparing the absorption of quinoid dyes derived from mono-, di-, and tri-phenylmethane Hantzsch made an important discovery. Baeyer had previously demonstrated that while quinoid monoamino-salts are strongly colored they cannot be regarded as true dyes and that the distinct characteristics of a dye appear only after the introduction of a second amino group. This was somewhat difficult to explain in view of the fact that the introduction of a third amino group did not have the effect of further intensifying the color of the dye as was to be expected from an auxochrome group but, on the contrary, actually played the

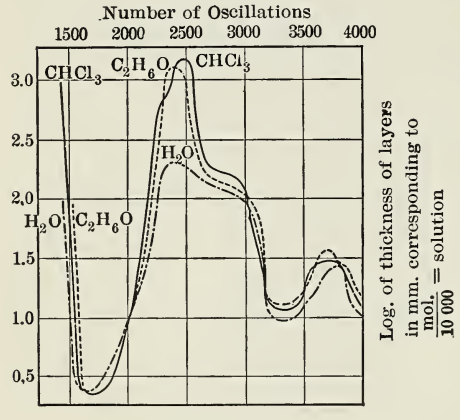


Fig. 3.

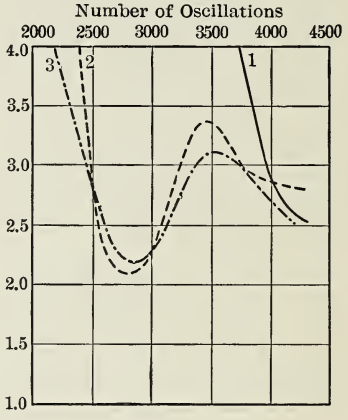
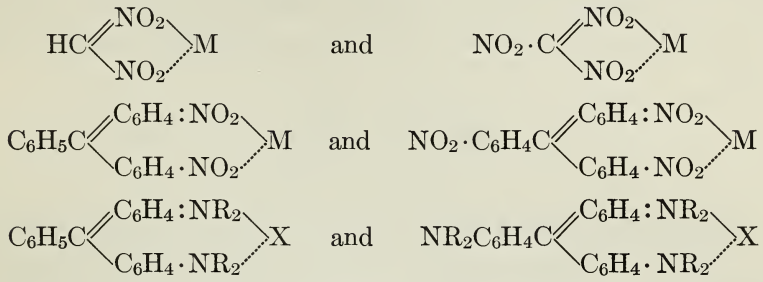


Fig. 4.

part of a weak hypsochrome. Similar observations were made by Hantzsch and F. Hein in connection with a study of the alkali salts of nitromethane and nitrotriphenylmethane. Thus mononitromethane forms colorless salts which show no absorption in the region of the penetrable ultra-violet while dinitromethane, on the other hand, forms yellow salts which are characterized by strongly banded absorption (Fig. 4). The introduction of a third nitro group into the molecule, on the other hand, produces nothing which even approximates the radical change induced by the introduction of the second nitro group. In other words salt formation in the case of dinitro and diamino derivatives of triphenylmethane is attended by marked changes in optical properties which cannot be accounted for on the basis of the older conceptions of the so-called theory of auxochromes.

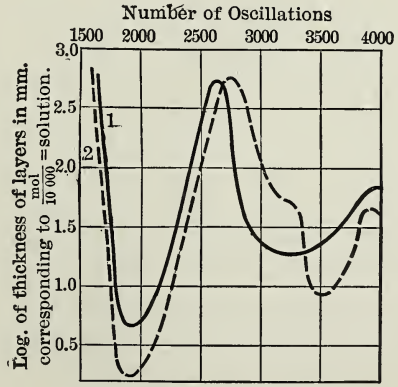
It would seem to follow from a consideration of these facts that only two nitro or two amino groups play an important part in the production

of color during salt formation and that in cases where a third such group is present in the molecule its rôle is distinctly subordinate. In other words the chromophore group may in every instance be assumed to result from the interaction of two and only two amino or nitro groups. This conception finds expression in the so-called *conjunction formulas* which have been introduced by Hantzsch to represent these dyes:



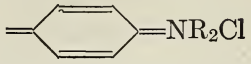
These formulas assume that the difference in the form of union of the two conjugated nitro or amino groups,—which is shown by the fact that one forms part of a quinoid grouping while the other does not,—involves no fundamental change in the constitution of these groups which are in all other respects identical. No special form of expression is, therefore, necessary to indicate this difference or to differentiate these groups from the third nitro or amino group which differs from both of the other two in that it does not form an integral part of the conjugated complex and is not in direct union with the acid or metallic ion.

It has been observed that the absorption curves of the simplest aminoazobenzenes and the simplest fuchsines very closely resemble each other.

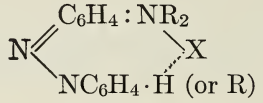


1. Dimethylaminoazo benzene.
2. Fuchsine. Both substances in very dilute HCl.

This is not very surprising, however, in view of the fact that both classes of dyes contain the chromophore grouping



and may, therefore, be supposed to form conjugated quinoid complex salts. In the case of the azo dyes the acid ion is assumed to be simultaneously in union with the quinoid amino group and a second amino group:



In summary it may be said that this interpretation of dye formation is significant because according to it the optical properties of three important groups of dyes may be regarded as due to the same general causes, viz.,

1. The presence in the molecule of a quinoid complex containing nitrogen which is strongly colored and which plays the rôle of a chromophore.

2. The presence of a second group containing nitrogen which is not itself colored but which when coupled with a quinoid group plays the rôle of a strong auxochrome.

The well-known fact that all of the above dyes are materially changed by the action of acids may be accounted for on the basis of this conception by assuming that the acid enters into chemical combination with the nitrogen residue and thus destroys its power of forming an inner complex salt.

The fact that the introduction of a third amino or nitro group into triphenylmethane and its derivatives produces a lightening of the color and not a deepening as might be expected, may be explained by a slight modification of H. Kauffmann's theory.[1] It will be recalled that halochromism has been investigated from two entirely independent points of view. On the one hand attention has been concentrated upon the phenomenon of salt formation and an effort has been made to ascertain the causes which under varying conditions, operate to produce salts while, on the other hand, attention has been concentrated upon the phenomenon of color and effort has been directed to ascertain its cause. Baeyer and Villiger [2] were able as early as 1902 to define the character of a salt in terms of the ease with which it tends to hydrolyze and they even

[1] Ber., **52**, 1422 (1919).
[2] Ber., **35**, 3019 (1902).

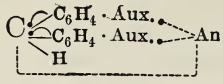
formulated certain general rules in regard to salt formation. The phenomenon of color does not, however, conform to the same rules since it has been observed that while a deepening in color is sometimes proportional to the basicity of a substance, the opposite is also sometimes true. Indeed the investigation of halochromism in the case of the triphenyl carbinols convinced Kauffmann that salt formation and color represent entirely independent phenomena and that each is governed by its own particular laws.

In applying the conception of the decentralization of chemical function to the colored salts of the triphenyl carbinols, Kauffmann assumes that the cation does not necessarily have its seat on a single atom but that the total positive charge is frequently made up of smaller units which originate respectively on different atoms located in different parts of the molecule. Since all such fractions of a given cation may be supposed to represent small positive charges, they will mutually repel each other. This conception is embodied in Kauffmann's first principle governing the partition of cation valencies, "cationic valence parts do not saturate each other."

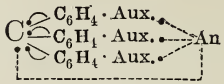
According to Kauffmann's principle of shifting relationships the different components of any molecule are in a condition of constant flux and it may, therefore, be supposed that the parts which together constitute the total charge of the positive complex do not represent fixed and definite values but that they vary incessantly,—an increase in the positive value of the charge at certain points in the molecule corresponding to a decrease at other points. Kauffmann assumes, moreover, that cationic partial valencies may be present in the molecule even when the molecule in question does not possess the power of ionic dissociation. This follows from the fact that inner complex salts exist in which cationic partial valencies are neutralized inside the molecule. The presence of valencies of this type cannot be detected by means of electrolytic measurement and is only apparent from a study of the shifting relationships within the molecule. Kauffmann's second principle in regard to cationic partial valencies is based upon the above considerations and supposes—"those partial valencies which act in competition with cationic valencies are themselves cationic in character."

Auxochromes, according to Kauffmann, represent groups of atoms which possess cationic partial valencies. This follows from the fact that the ammonium valency of the nitrogen in the amino group, for example, is not required for the saturation of the phenyl group and a certain fraction of the total affinity of the nitrogen atom is, therefore, available in the form of free positive partial valencies which may be exercised in saturating other positions within the molecule. This con-

ception finds expression in the following formulas for the colored salt of tetramethyldiaminobenzhydrol (I) and crystal violet (II).

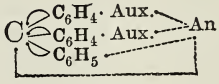


I



II

where the ionic partial valencies are represented by means of dotted lines while other fractions of the total affinity of any atom which are less than a so-called unit valence are represented by curved lines terminating in dots. According to the latter formula the fourth valency of the methane carbon atom is represented as broken up into a number of parts which are distributed among the three phenyl groups and the anion. Since depth of color is supposed to correspond to the degree of decentralization of valency crystal violet (II) might be expected to possess a deeper color than tetramethyldiaminobenzhydrol but as a matter of fact this is not the case. Kauffmann accounts for this apparent discrepancy by his third principle in regard to cationic partial valencies according to which—"the decentralization of ionic charge does not function in the production of color." This is further illustrated by the fact that malachite green (III).



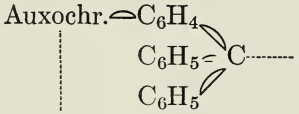
III

exhibits greater decentralization of its cationic valence than does the salt of tetramethyldiaminobenzhydrol, but less than the salt of crystal violet. Here again these properties seem to bear no relation to the optical properties of these respective substances.

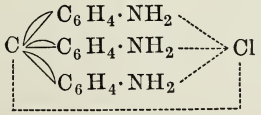
In summary it may be said that while a decentralization of the cationic charge has been observed to correspond to an increase in the basic properties of the methane carbon atom, this is not proportional to a deepening in the color in the case of certain compounds. From this it would seem to follow that the methane carbon atom is not the seat of color in these substances. Similar relationships exist in the case of a number of different compounds which have been investigated by Hantzsch and even in certain instances where OCH_3 replaces $N(CH_3)_2$ in the molecule. To explain the phenomenon of color Kauffmann supposes that the seat of color is located on a ring carbon atom. This assumption holds in the case of nitro as well as in the case of amino derivatives of triphenylmethane. Salts of triphenyl carbinol, for

example, contain three distinct centers of color, namely, the three ring carbon atoms which are in union with the methane carbon atom.

H. Kauffmann [1] carries the analysis further and is of the opinion that the basic properties which have been observed in the case of these substances are not actually properties of the methane carbon atom but that they denote a general decentralization of the chemical functions not only of the central carbon atom but also of other atoms in union with it. Kauffmann assumes that the exchange of affinity within the molecule regulates the degree of basicity and simultaneously the color of any given compound. In the case of triphenyl carbinol, for example, the basicity is increased by the introduction of auxochrome groups in favored positions and is most marked when two such groups occupy *para* positions with reference to each other. This relationship may be expressed by means of the following diagram



in which the dotted lines that are supposed to represent the fourth valency of the carbon atom decrease in size in proportion to the strength of the particular auxochrome. The ability of the methane carbon atom to hold a fourth atom or group is represented as weakened by the introduction of substituents in the place of hydrogen in the benzene ring, and it, therefore, follows that an increase in the number of auxochrome groups will be accompanied by a decrease in the stability of the union between the methane carbon atom and a fourth atom or group. This will become apparent in a tendency to ionization,[2] and trianisylmethyl chloride, for example, will be found to possess perfectly definite salt-like properties. In the case of parafuchsine the decentralization of valency on both the carbon and the chlorine atom may be assumed to be very great, as shown by the following diagram:



The interdependence of these two atoms is obvious and can be followed experimentally since the breaking up of the total affinity of the carbon atom into a number of relatively small partial valencies has long been

[1] Ber., **46**, 3794 (1913).
[2] Ber., **46**, 3794 (1913).

associated with the phenomena of color, while the same condition in the case of the chlorine atom has been associated with the phenomena of ionization.

Halochromism has been observed in widely separated fields of organic chemistry but even the most divergent groups of colored compounds have been interpreted and related by means of Pfeiffer's theory, which may now be considered in some detail.

Many colorless or weakly colored compounds dissolve in mineral acids to give solutions which are intensely colored. Dibenzal acetone, for example, and other allied substances behave in this way. The color of the product depends in any given case upon the character of the substituted phenyl group and of the acid radical. Thus dibenzal acetone reacts with concentrated sulphuric acid to give a product which is reddish orange, while with hydrochloric acid the product is dark red, and with hydrogen iodide, black. In each case the color is destroyed upon the addition of water and dibenzal acetone is precipitated. The compounds which are formed in this way have been shown to be addition products of dibenzal acetone with one or more molecules of acid. H. Stobbe has undertaken a series of very exact investigations which tend to show that in the case of hydrochloric acid such addition products have the general formula ketone$+x$HCl, and that the value of x varies inversely as the temperature.

Variations of color due to substitutions in the phenyl group are shown in the following table:

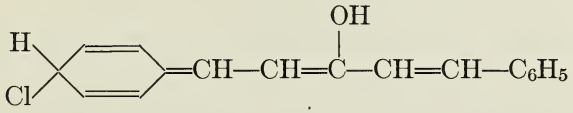
Ar·CH=CH—CO—CH=CH·Ar′·

Ar	Ar′	Moles HCl at		Color of Salt at
		15°	−75°	15°
C_6H_5	C_6H_5	2	4	Red
$CH_3OC_6H_4$ (1–4)	$CH_3OC_6H_4$ (1—4)	2	5	Violet black
$C_2H_5OC_6H_4$ (1—2)	$C_2H_5OC_6H_4$ (1—2)	2	4	Violet
C_6H_5	$CH_3OC_6H_4$	1.5	4	Reddish violet
C_6H_5—CH=CH—	C_6H_5—CH=CH—	2	4	Violet black

That the relation which exists between colored compounds of this type is complicated may be seen from the fact that it is possible to prepare both a colored and a colorless addition product by the addition of one molecule of dibenzal acetone and one molecule of hydrochloric acid and that two products are also formed by the addition of one molecule of dibenzalacetone and two molecules of hydrochloric acid. In general

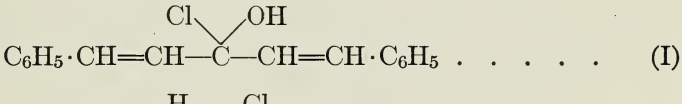
two series of salts are possible,—one colorless, the other colored. It has been observed, moreover, that these two series are quite separate, and that the colored salts cannot be obtained from their colorless isomers.

A number of theories have been advanced as to the structure of these substances. It does not seem probable that they represent additions of hydrochloric acid to the unsaturated carbon linkages since this would mean a decrease in the number of conjugate systems present in the molecule and would serve to weaken the color by lessening the number of chromophores. Baeyer and Villiger [1] have suggested that colored salts of this type might possess quinoidal structure:

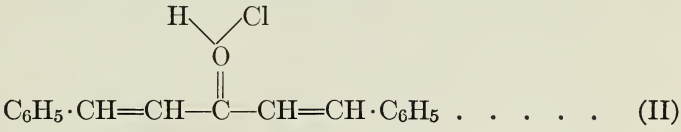


but an objection to this is to be found in the fact that the above configuration is quinolic and not quinoid and that the formula does not, therefore, serve to explain the color of the compound.[2]

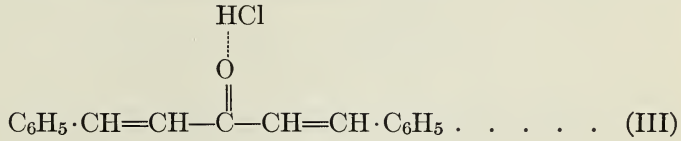
Another explanation of the phenomenon presupposes addition of hydrochloric acid to the carbonyl group in one of three ways:



(I)



(II)



(III)

Straus and Caspari [3] have recently succeeded in preparing substances corresponding to the first formula, and have shown that such products are entirely colorless and are not decomposed by the action of alkali. It might therefore be assumed that the colored compounds under consideration correspond to the second formula and that they, therefore, belong to the general class of oxonium salts.

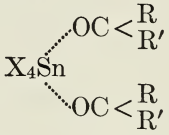
[1] Ber., **35**, 1191 (1902).
[2] See Vorländer and Mumme, Ber., **36**, 1482 (1903).
[3] Ber., **40**, 2689 (1907).

P. Pfeiffer [1] has recently made a series of special investigations in regard to halochromism among ketones. Since phenomena of this type have been observed most frequently in the case of substances which contain carbonyl groups, Pfeiffer decided to study the subject systematically and to this end prepared a large number of addition products of the general formula:

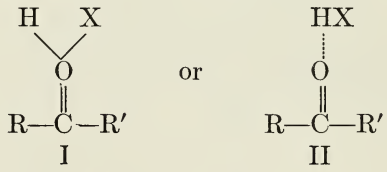
$$SnX_4 \cdot 2RCOR'$$

where R equals phenyl, methoxyphenyl, cinnamyl, or furyl, and R′ equals H, CH_3, OH, OC_2H_5 or NH_2. These substances crystallize well and may be readily prepared by treating $SnCl_4$ and $SnBr_4$ with aldehydes, ketones, acids, esters, and amides.

In terms of Werner's theory compounds of this type may be regarded as belonging to the same general class as other double salts of tin. Since the coordination number of tin is six such substances may be assumed to possess the formula:



These substances resemble the acid addition products in all essentials and the latter may therefore be assumed to possess a similar configuration. The structure of compounds formed by the addition of acids to carbonyl narrows itself down to two possibilities, viz.,

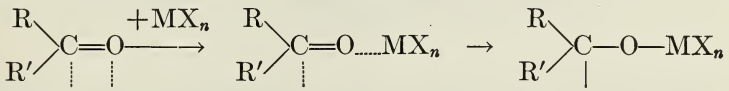


but since the former (I) fails to account for the striking similarity in properties which has been observed in the case of the two types of molecular compounds which are formed by the action of acids and metallic salts respectively, it has been discarded in favor of the second formula (II).

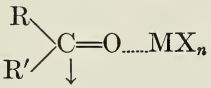
The mechanism of this addition has been explained by Pfeiffer and has already been referred to in a previous chapter. In brief it assumes that the molecule of acid or salt adds to the free affinity on the oxygen

[1] Annalen der Chemie, **370**, 99 (1909); **376**, 285 (1910); **383**, 92 (1911); **404**, **1** (1914); **412**, 253 (1916); also compare F. Straus and H. Blankenhorn, Annalen der Chemie, **415**, 232 (1918).

atom and that this union, which is at first very unstable, changes to one of greater stability, thus engaging a greater fraction of the total affinity of the oxygen. The change is accompanied by the evolution of heat and by a corresponding increase in the free affinity of the adjacent carbon atom, the latter gradually approaching a trivalent condition as more and more of its bound chemical energy is released by the carbonyl oxygen atom. Since this condition is essentially the same as that which has been observed in the case of triphenylmethyl its existence is to be associated with the appearance of color. Pfeiffer [1] originally expressed these conceptions by means of the following symbols:



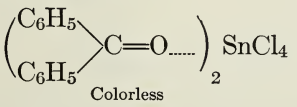
but he has recently modified the formula for the product to



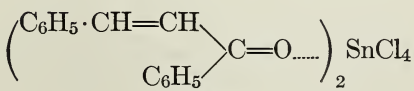
The arrow serves to indicate the presence of free affinity on the carbon atom and, therefore, accounts for its increased chemical reactivity.

According to Pfeiffer other chromophore groups such as C=N, C=C, N=O, etc., behave in exactly the same way as carbonyl and may, therefore, be responsible for the phenomenon of halochromism. In all cases the appearance of color in a substance can be referred to the presence of an unsaturated atom in its molecule and in this way the relationship which exists between color and chemical constitution is brought into harmony with modern physical conceptions in regard to the cause of the phenomenon.

It has been noted that the addition products which are formed by the action of $SnCl_4$ and HCl upon ketones are in some cases colorless while in other cases the color varies from yellow to orange-red, to bordeau-red, to black, as for example,

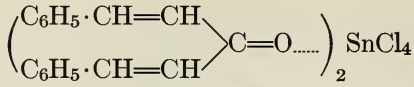


Colorless

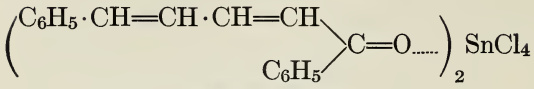


Yellow

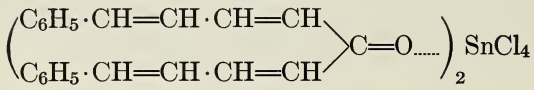
[1] Annalen der Chemie, **383**, 93 (1911).



Reddish orange



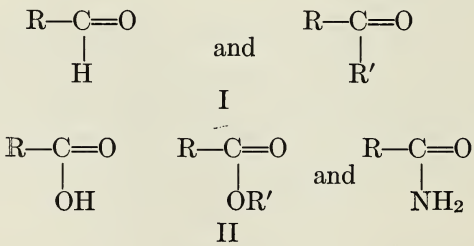
Reddish orange



Black.

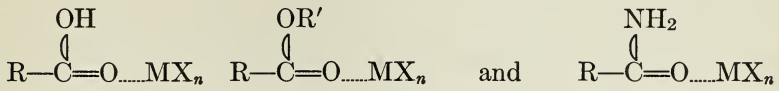
Such differences in color may be readily explained in terms of Pfeiffer's theory since the above formulas indicate that depth of color bears a direct relation to the number of ethylene groups which are present in the molecule of any given ketone. It should be noted that the ethylene groups in addition to being unsaturated themselves may act to increase the unsaturation of the carbonyl carbon atom. Indeed the presence of a number of ethylene groups in a given molecule may release so much of the bound chemical energy of this atom as to cause it to approximate the trivalent condition.

A marked difference has been observed in the halochromic properties of aldehydes and ketones as compared with acids, esters, and acid amides, the former giving much more deeply colored addition products with $SnCl_4$ than the latter. This, too, may be readily explained in terms of Pfeiffer's theory if the general formulas for these five classes of substances are compared:

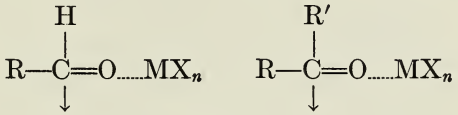


If X is used to represent R′, H, OH, OR′, and NH_2 it is obvious that the unsaturated character of the carbonyl group will depend upon two factors, namely R and X, and that if R remains constant, it will vary solely according to the nature of X. If now X is represented by such unsaturated groups as OH, OR′, NH_2, NR_2, etc., it follows that the

effect will be to decrease the unsaturation of the carbonyl group. It is easy to understand by means of the following formulas:

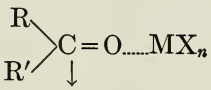


why the addition products which are formed by the action of $SnCl_4$, HCl, etc., upon acids, esters, and acid amides should be colorless or only slightly colored. These formulas are in marked contrast to those which are used to represent the atomic relationships in the corresponding addition products formed by aldehydes and ketones:

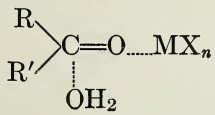


and which serve to explain the relatively deep color of such compounds.

These speculations lead to other interesting conclusions which may be noted at this point. If the colored addition products which are formed by the action of metallic halides upon unsaturated ketones actually possess the formula



they should by virtue of their free affinity be capable of entering into chemical combination with other molecules such as water, alcohol, etc., to give tertiary compounds of the general formula

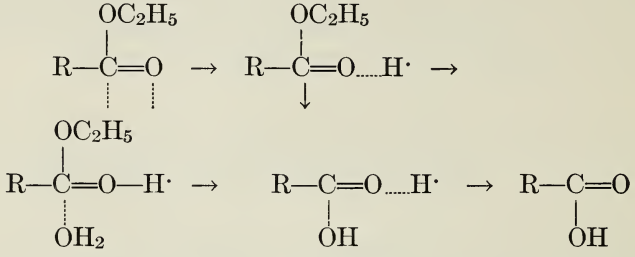


These deductions have been verified experimentally by Pfeiffer [1] who has succeeded in preparing substances of this type and who has found that, as was to be expected, they are actually lighter in color and correspondingly more saturated than the parent substances.

Pfeiffer has carried his analysis still further and attempts to explain the catalytic action of hydrogen ions in the saponification of esters on

[1] Annalen der Chemie, **383**, 119 (1911).

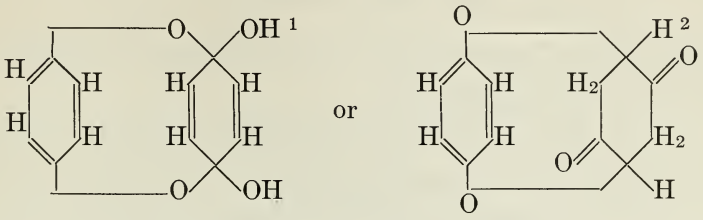
the assumption that tertiary molecules of the above type form as intermediate products during the progress of the reaction. He supposes that the primary action consists in addition of the hydrogen ion in a coordinate position to the oxygen atom of the carbonyl group. This is accompanied by an increase in the free affinity of the adjacent carbon atom and is followed by the addition of a molecule of water and the formation of a tertiary compound. The latter then decomposes with the separation of one molecule of alcohol and the formation of the free acid:



It is scarcely necessary to add that Pfeiffer's theory offers a satisfactory explanation for the phenomenon of halochromism which has been observed in connection with the action of sulphuric, nitric and perchloric acid upon triphenyl carbinol and with the action of metallic halides upon triphenylchlormethane. As in the preceding cases color is supposed to be due primarily to the presence of free affinity upon the methane carbon atom and not to the quinoid configuration of a benzene ring.

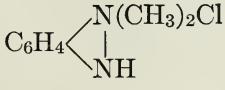
The application of this theory to the interpretation of the phenomenon of color in the case of the quinhydrones is of especial interest and may be considered briefly at this point. This important group of organic compounds represents products which are obtained by the direct addition of quinones to phenols and amines, and the question of their constitution has been a perplexing one for many years. The best known example of a substance of this type is quinhydrone. This substance is formed by the interaction of quinone and hydroquinone and has the formula $C_6H_4O_2 \cdot C_6H_4(OH)_2$. It is dark green in color although quinone is yellow and hydroquinone is colorless. Substances of this class may in general be described by saying that they are much more deeply colored than their components and that they dissociate into these components with great ease. These characteristics had not been accounted for in a satisfactory way by any of the earlier theories which were advanced to explain their constitution. For example, it was at first supposed that addition took place as a result of the mutual saturation of carbonyl and ethylene double bonds located on the quinone and

hydroquinone molecules respectively and that the substance therefore possessed either one of two possible configurations, i.e.,



Both formulas suppose that the addition of the two molecules is effected by a saturation of two principal valencies and therefore neither affords a satisfactory explanation for the color of the substance nor for the ease with which it dissociates into its components.[3] To overcome this objection it was then assumed that the addition of the two components takes place as the result of the mutual saturation of partial valencies on the two molecules and that quinhydrones may thus be regarded as typical examples of molecular compounds. This conclusion seemed at the time to afford a satisfactory explanation of the phenomena and was in general harmony with the experimental data obtained as a result of the investigations of Urban,[4] Willstätter and Piccard,[5] Kurt H. Meyer,[6] Schlenk [7] and others. The question has recently received further elucidation, but before these latest developments can be considered it will be necessary to review the researches of Willstätter and his students in some detail.[8]

In 1879 C. Wurster [9] discovered two dyes, one of which was red and the other was blue, corresponding respectively to the formulas $C_8H_{12}N_2Br$ and $C_{10}H_{15}N_2Br$. Later A. Bernthsen [10] discovered that the red dye resembled quinone in some of its properties and he, therefore, gave it the quinoid formula



[1] L. Jackson, Ber., **28**, 1614 (1895).

[2] Th. Posner, Annalen der Chemie, **336**, 85 (1904).

[3] Compare Ber., **43**, 3603 (1910); **44**, 1503 (1911).

[4] Monatsh. Chemie, **28**, 299 (1907).

[5] Ber., **41**, 1458 (1908).

[6] Ber., **43**, 157 (1910).

[7] Annalen der Chemie, **368**, 271 (1909).

[8] Ber., **37**, 1494, 3761, 4605 (1904); **38**, 1232, 2244, 2348 (1905); **39**, 3474, 3482, 3765 (1906); **40**, 1406, 1432, 2665 (1907); **41**, 1458 (1908).

[9] Ber., **12**, 1803, 1807, 2071 (1879); also **19**, 3195, 3217 (1886).

[10] Annalen der Chemie, **230**, 162 (1885); **251**, 11, 49, 82 (1889).

which was later slightly modified by Nietzki [1] to

$$HN{=}C_6H_4{=}N(CH_3)_2Cl$$

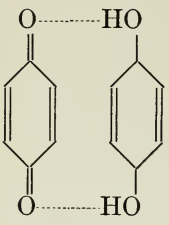
In either case the red compound may be regarded as belonging to the general class of quinonium salts.

Following this Willstätter and his students undertook a systematic investigation of quinoids. They succeeded in preparing the simplest quinone-imides and discovered that these are not intensely colored as was to be expected from theoretical considerations, but are on the contrary either colorless or yellow. For example $O{=}C_6H_4{=}NH$ and $NH{=}C_6H_4{=}NH$ are colorless, $O{=}C_6H_4{=}NCH_3$ is slightly yellow in solid form and bright yellow in solution, and $CH_3N{=}C_6H_4{=}NCH_3$ is colorless in solid form and bright yellow in solution. When these substances were compared with the red compound which had been discovered by Wurster and which was supposedly so closely related to them in structure, it was discovered that the difference was so great, both as to shade and intensity of color, as to preclude the possibility of a similar constitution. A doubt as to whether the red salt was a true quinoneimide had been voiced by Willstätter and Pfannenstiel [2] as early as 1905, but it was not until three years later that Willstätter and Piccard [3] actually discovered that Wurster's salt was not a true quinoneimide (holoquinoid) but a semi-quinoneimide (meriquinoid). They then succeeded in preparing the holoquinoid of *p*-aminodimethylaniline and found that it was entirely colorless but that on partial reduction it readily passed into the red meriquinoid. The latter could also be prepared by the combination of one molecule of leuco-base (*p*-aminodimethyl aniline) with one molecule of holoquinoid.

These facts lead to the conclusion that Wurster's salt represents a transition or intermediate product between quinones and hydroquinones, or, in other words, belongs to the class of quinhydrones. This discovery helps to substantiate an opinion previously expressed by Kehrmann in regard to colorless and colored di-imides, namely, "many of the deeply colored substances of quinoid character which are formed by the oxidation of simple amines and which on reduction revert to them again, are in fact quinhydrones." In order to account for the two most important characteristics of these substances, viz., their color and the ease with which they dissociate, Willstätter and Piccard assume that quinhydrones are formed as the result of the

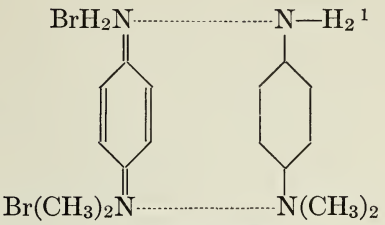
[1] "Organische Farbestoffe," 5th Ed., 1906 p. 199.
[2] Ber., **38**, 2244 (1905).
[3] Ber., **41**, 1462 (1908).

mutual saturation of the partial valencies of their components as represented by the following scheme:



Quinhydrone.

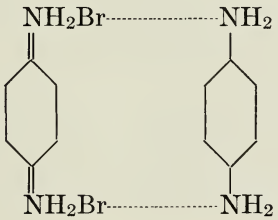
I



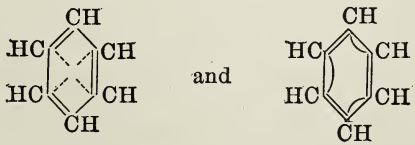
Wurster's red salt.

II

Since then Piccard has succeeded in preparing the simplest dye of this type, namely:



An objection to this interpretation is to be found in the fact that Wurster's salt differs markedly from the quinhydrones in that it is a much more stable compound. Although it dissociates in acid solution, it dissolves in water without any appreciable decomposition into its components while quinhydrones, on the other hand, break down very readily on solution. This important difference may be explained by supposing a corresponding difference in the constitution of the molecules of two types of meriquinoids (I and II). The red salt, being the more stable in its properties, may be assumed to possess the more saturated molecule, and this difference in degree may be visualized as corresponding roughly to the difference in the degree of saturation represented respectively by the following two formulas for benzene:[2]



[1] Compare Annalen der Chemie, **381**, 351 (1911).

[2] Ber., **41**, 1458 (1908); see also Kehrmann, Ber., **41**, 2340 (1908).

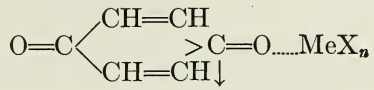
Just how the saturation of free affinity takes place in the case of the substances under consideration remains a question, although there is at the present time much speculation in regard to the constitution of the meriquinoids. It has been suggested that the two components exist in a condition of dynamic equilibrium with reference to each other and that the pronounced color of this type of compound as compared with the very slight coloration of its components (quinones and imines respectively) may thus be accounted for on the basis of *isorropesis*, or, in other words, a make-and-break in the linkage of residual valencies. While this term has usually been applied to an *intra*-molecular condition it may be extended to include an *inter*-molecular condition such as is represented in the recurrent making and breaking of linkages between different molecules. In either case vibrational disturbances are produced. These are supposed to occasion molecular oscillations which in terms of Hartley's theory cause the phenomenon of color. Since the stability of certain solutions of meriquinonium salts as compared with solutions of quinhydrones is explained as due to a relatively greater degree of saturation, it follows that the color of these substances must be assumed to be due to isorropesis of the *intra*-molecular rather than of the *inter*-molecular type, for the latter conception is obviously possible only on the assumption of a relatively loose union between the component molecules.

Interpretations of this kind may be applied not only to Wurster's red salt but also to fuchsine, which closely resembles it in the color of its aqueous and acid solutions and in the color of its compounds. In general, it may be assumed that substances of this type are formed by the union of one molecule of a weakly colored ammonium salt with one or two molecules of amines and that they are usually meriquinoid in structure.[1] H. Kauffmann[2] explains the phenomenon in terms of his particular conceptions by assuming that the dotted lines, which are used in the above formulas to express partial valencies, indicate a breaking up ("Zersplitterung") of affinity. As has been noted such a condition of split affinity is supposed by Kauffmann to account for the phenomenon of color.[3]

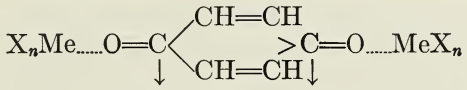
The investigations of Kurt H. Meyer[4] in the field of the so-called phenoquinones aided materially in the further elucidation of this problem. Phenoquinones are formed by the addition of phenols to quinone and resemble the quinhydrones in their general properties. In the

[1] Ber., **41**, 1458 (1908); also Kehrmann, Ber., **41**, 2340 (1908).
[2] "Die Valenzlehre," p. 510.
[3] Compare Werner, Ber., **42**, 4324 (1909).
[4] Ber., **41**, 2568 (1908); **42**, 1149 (1909); **43**, 157 (1910).

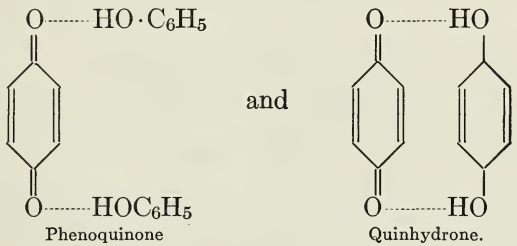
course of their investigation Meyer made the important discovery that quinones possess the power to combine with other substances, such as acids and metallic halides, with which they form salt-like addition products. The latter are relatively deeper in color than the corresponding quinones and readily dissociate into their components. In short quinones in common with other ketones exhibit the phenomenon of halochromism. In the case of benzoquinone, for example, metallic addition products of this type may be represented as possessing, in terms of Pfeiffer's theory the formulas:



and



The application of this discovery to the problem of the constitution of quinhydrones was developed by Pfeiffer following the discussion of certain objections which had been raised to the Willstätter-Piccard formulas:



Phenoquinone

Quinhydrone.

The question arose as to the particular atoms in the molecule which served to unite the two components. While there was little doubt that oxygen represented the seat of the partial valencies in the quinone molecule, the seat of the corresponding valency in phenol was uncertain. In order to decide the question as between hydrogen and oxygen of the hydroxyl group, Pfeiffer attempted to prepare addition products by the action of phenyl ethers upon quinone. His experiments proved successful and in the case of $C_6H_4(OCH_3)_2$, for example, he obtained a deeply colored readily dissociable product which resembled quinhydrone in all essentials. This seemed to settle the question in favor of the oxygen atom but it was opened again almost immediately by the discovery by Haakh [1] and Pfeiffer [2] that similar addition products could be

[1] Ber., **42**, 4595 (1909).

[2] Annalen der Chemie, **404**, 5 (1914).

prepared by the action of aromatic hydrocarbons upon quinones. Stilbene, fluorene, naphthalene and anthracene when melted with quinone and chloranil give deep colorations, although as yet it has been impossible to isolate these products. A red crystalline substance was, however, separated as a product of the addition of durene to chloranil and a similar substance was obtained as a result of the reaction between durene and bromanil. These substances have been purified and analyzed and correspond respectively to the formulas:

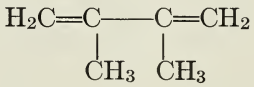
$$C_6Cl_4O_2 \cdot 2C_6H_2(CH_3)_4 \quad \text{and} \quad C_6Br_4O_2 \cdot 2C_6H_2(CH_3)_4$$

They are therefore in all respects directly analogous to the phenoquinones.

It follows from this discovery that the seat of the free affinity on the phenol molecule is neither the hydrogen nor the oxygen of the hydroxyl group and the discussion, therefore, shifts to a decision between the hydrogen and the carbon of the benzene ring. Since hexamethylbenzene combines with chloranil to give a reddish brown addition product having the formula

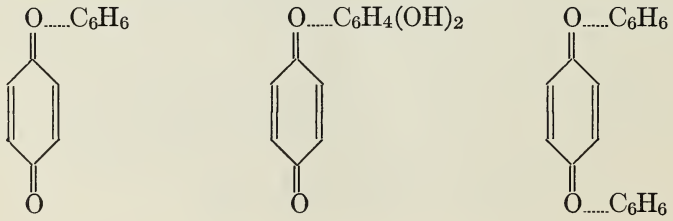
$$C_6Cl_4O_2 \cdot C_6(CH_3)_6$$

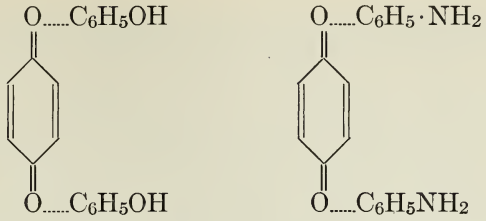
and since chloranil dissolves in dimethylbutadiene,



to give an orange colored solution, it may be assumed that unsaturated carbon atoms represent the seat of the free affinity.

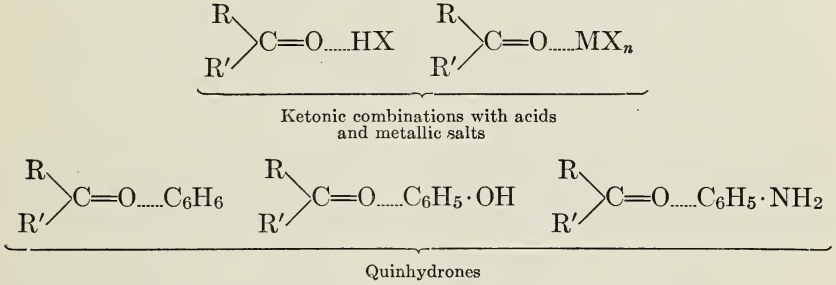
In general it may be said that, according to the conceptions of Werner's theory, the formation of quinhydrones takes place as a result of the saturation of partial valencies present on the oxygen of the carbonyl group in the quinone molecule, by other valencies which are present on the unsaturated carbon atoms of the benzoid molecule. The two classes of addition products which may be obtained in any case are represented by means of the following formulas:



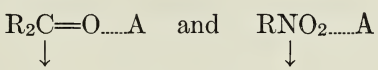


The fact that the quinone oxygen atom appears to be coordinately univalent is not surprising but the fact that the benzene ring behaves in the same way is rather remarkable.[1]

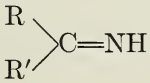
That the phenomena may be included under the general head of halochromism is obvious from a comparison of the type formulas



The applications of the theory of halochromism have been by no means exhausted as a result of the present discussion of addition reactions which involve the carbonyl group. Corresponding colored addition products may be obtained if nitro groups are substituted for carbonyl as for example,



where A is used to represent any adding molecule. It even seems as if halochromism were a property which is possessed in common by all unsaturated groups, since unsaturated hydrocarbons, ketimines,



triaryl halides, azo-compounds, tetraaryl-hydrazines, etc., etc., all react with acids and metallic halides to give highly colored and readily dissociable addition products. In every case the deepening in color

[1] See P. Pfeiffer and T. Böttler, Ber., **51**, 1828 (1918) for the more recent developments along these lines.

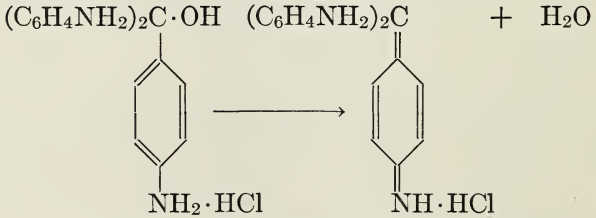
may, in terms of Pfeiffer's theory, be assumed to be due to a considerable increase in the free affinity of some one atom which is present in the molecule. The mechanism of the process is always described in the same simple way by supposing that the saturation of a partial valency in one part of the molecule leads to a lack of balance in the energy relationships in some other part of the molecule and that this frequently takes the form of a high degree of unsaturation at some one given point. This theory, together with the corollary that increase in the free affinity of an atom is accompanied by an increase in its power to act as a chromophore, offers a satisfactory general explanation for the phenomenon of halochromism. It should again be noted, however, that the amount of free affinity which the arrow represents in these formulas

$$\underset{\downarrow}{R\cdot NO_2\cdots\cdots HX} \qquad \underset{\downarrow}{R\cdot NO_2\cdots\cdots MX_n} \qquad \underset{\downarrow}{R\cdot NO_2\cdots\cdots C_6H_6} \qquad \underset{\downarrow}{RNO_2\cdots\cdots C_6H_5\cdot OH}$$

$$R\cdot NO_2\cdots\cdots C_6H_5\cdot NH_2$$
$$\downarrow$$

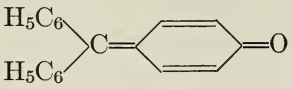
varies not only with the character of A but also with the nature of the substituents (OH, OCH_3, NH_2, CH=CH, etc.), which are present in R and that such variations are accompanied by corresponding changes in color.[1]

The application of Pfeiffer's theory to the case of derivatives of triphenyl carbinol must now be considered. In general it may be said that while the relationships are much more complicated in the case of these substances than in the case of any which have yet been considered, it seems probable that in some cases at least color is due to a quinoid configuration of the molecule. Baeyer found, for example, as the result of an exhaustive investigation of a large number of derivatives of triphenyl carbinol, that all oxy- and amino-derivatives resemble the parent substance in being entirely colorless. Since the appearance of color in these compounds is associated in every case with the elimination of one molecule of water, the simplest explanation of the phenomenon is one which supposes that this process involves a change from the benzoid to the quinoid state:

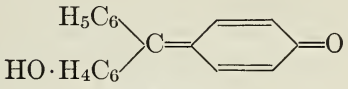


[1] Annalen der Chemie, **412**, 253 (1916).

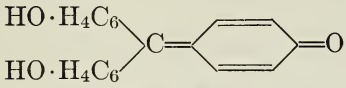
The various types of dyes which belong to this group have therefore been formulated in the following way:



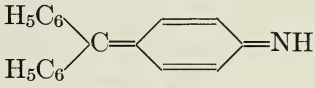
Fuchsone



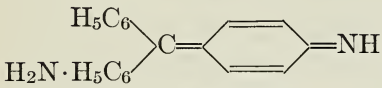
Benzaurine



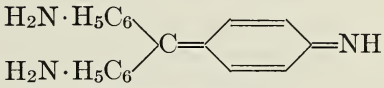
Aurine



Fuchsoneimide

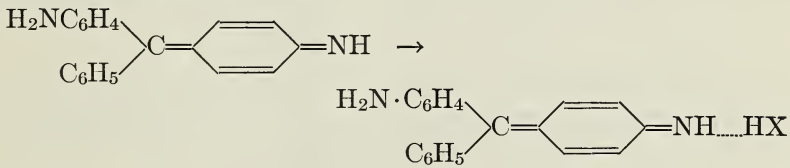


Aminofuchsoneimide



Diaminofuchsoneimide

Of these substances the fuchsoneimides stand somewhat apart from the others in that they possess a slightly different brown to orange color and when treated with acids they form addition products which possess every variety of color. Since in this case a weakly colored ketoneimide passes into a highly colored molecular compound on the addition of acids, the phenomenon represents a clear case of halochromism and may be formulated as follows:



Thus even in the triphenylmethane series certain types of colored compounds must obviously be accounted for on the basis of Pfeiffer's theory.

The fuchsones and oxyfuchsones also form intensely colored addition products with acids and metallic salts but these differ from those which have just been described in the case of the fuchsoneimides in that they are about the same shade as the parent substance or even lighter as is illustrated, for example, in the salts of benzaurine and aurine. From this it would seem to follow that the fuchsones and oxy-fuchsones must differ in constitution from the ordinary types of unsaturated oxyketones.

The relation which exists between the absorption spectrum of a substance and the chemical constitution of its molecule has been discussed at some length in a preceding chapter where it was pointed out that all changes in the atomic relationships within the molecule are accompanied by corresponding changes in absorption. Such changes, in

the greatest possible variety from the finest to relatively the crudest, have been followed in connection with a study of the phenomenon of salt formation in the case of organic acids, and as a result many of the laws which govern these particular relationships have been discovered.[1] The graphic representation of changes in the absorption of a substance by means of absorption curves has led in the first place to the classification of all such changes under two heads:

I. Those in which the number and relative position of the absorption bands remain unchanged and where the general character of the absorption spectrum of the substance is unaltered. Under these circumstances changes in constitution are accompanied either by a shifting of the absorption band of the substance in the direction of longer or shorter wave lengths, or by an increase in the intensity of absorption.

II. Those in which the whole character of the absorption spectrum of the substance is fundamentally changed. For example, salt formation in the case of benzoic acid, its homologues and its substitution products is accompanied by a more or less pronounced shifting of the absorption curves of these substances in the direction of the shorter wave lengths and is accompanied by a simultaneous decrease in the intensity. In the case of phenol and its homologues, polyphenols, hydroxystilbenes, hydrooxyquinolines, etc., the effect of salt formation

$$C_6H_5 \cdot OH \rightarrow C_6H_5 \cdot ONa$$

is much more pronounced than in the preceding case and is accompanied by a shifting of the absorption curve in the opposite direction, i.e., in the direction of the longer wave lengths.[2]

Both types of neutralization are alike in that they are accompanied by only minor changes in the absorption spectrum of the substance and therefore, quite obviously fall within the category defined by Class I. In interpreting the change in constitution which is suffered by the molecule in the transformation of $C_6H_5OH \rightarrow C_6H_5ONa$, for example, it must be assumed that the oxygen atom maintains relatively the same general relation to the adjacent carbon atom before and after the change. In other words the amount of affinity with which this particular atom is bound to the carbon of the ring may vary considerably without fundamentally affecting the absorption of the substance—that is to say so long as this variation does not transcend the limits of what is commonly referred to as the benzoid condition of the molecule. As soon as this limit is passed, however, and the molecule as a whole

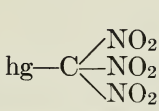
[1] J. Lifschitz, "Die Änderungen der Lichtabsorption bei der Salzbildung organischer Säuren," Stuttgart, 1914.

[2] Compare H. Ley, Zeitschr. physikal. Chemie, **94**, 405 (1920).

undergoes a rearrangement from the benzoid to the quinoid condition, the absorption spectrum suffers an abrupt and fundamental change. Such changes fall in the category of Class II and have frequently been observed during the process of salt formation.

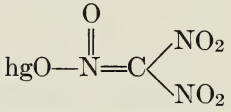
In all of the instances which have been cited changes in constitution, together with the accompanying changes in absorption, may be assumed to be due to differences in either the character or the distribution of the principal valencies and they must, therefore, be clearly distinguished from another type of change which results from the interaction of *partial* valencies and which must now be considered in detail.

In the case of nitro-compounds and other atomic complexes which are capable of undergoing intramolecular rearrangements, the change in color involved in salt formation becomes much more complicated. Thus, for example, according to Ley and Kissel [1] nitroform $CH(NO_2)_3$ gives a mercury salt $HgC(NO_2)_3$ which is colorless in solid form and which dissolves in ether and other indifferent solvents to give colorless solutions. On the other hand, this substance dissolves in alcohol and in water to give yellow solutions. Under these circumstances it is necessary to assume that it exists in two modifications, namely,



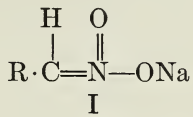
Pseudosalt, colorless, undissociated

and



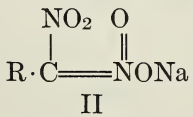
True salt, yellow dissociated

In the case of the nitroparaffines the relations are even more complicated. The mononitroparaffines are colorless and give colorless salts:



I

The dinitroparaffines are also colorless but give yellow salts:

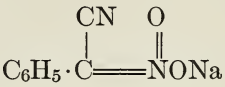


II

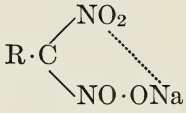
A comparison of the simplest formulas for these two classes of substances, as represented by I and II, would seem to show that the appearance of color in the second case is due merely to the substitution

[1] Ber., **32**, 1357 (1899); **38**, 973 (1905).

of a second nitro group. If this is true it might be supposed that the substitution of other negative groups, such as cyanogen, etc., would have the same effect, but the sodium salt of phenylcyan-nitromethane

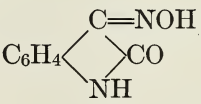


is actually colorless. From this it would seem to follow that the second nitro group plays a specific part in salt formation, and the theory has been advanced that its residual affinities are engaged in saturating residual affinities already present on the —NO·ONa group:



In order to arrive at a definite decision in regard to the constitution of these substances Hantzsch undertook a systematic investigation of the changes brought about by salt formation in the absorption spectra of a large number of organic compounds as, for example, nitro-, nitroso-, azo-, pyridine, quinoline, acridine and other bodies. The investigation proved to be one of considerable importance and led to a number of very interesting discoveries which may now be reviewed in some detail.

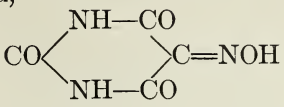
It may be assumed that in the formation of colored salts the color is conditioned either by the acid or by the metal or by both and Hantzsch, therefore, made a preliminary study of the action of colorless metals such as Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Zn, Cd, Pb, Ag, and Tl upon colorless acids. His results demonstrated that under normal conditions and in a great variety of instances, colorless acids combine with these metals to give colorless salts and that in cases where the acid has a definite color it reacts with these metals to give salts which possess the same color.[1] For example antibenziloxime is colorless and so are its salts with the above metals. Isatinoxime,



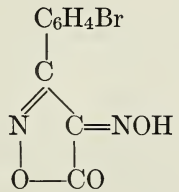
is yellow as are likewise its salts and esters. In such cases the organic acid is referred to as a monochromic acid.

[1] Ber., **42**, 967 (1909).

There are, however, a great many exceptions to this general rule. For example violuric acid,



which is itself colorless forms not only colorless salts with these metals but also yellow, red, blue, green and violet salts in great abundance and variety. Such an acid is referred to as a polychromic acid because it is capable of forming salts which are characterized by many different colors. Since these salts are believed by Hantzsch to be isomeric, the phenomenon is known as chromoisomerism. Other organic compounds have been observed to possess this property as, for example, mono- and di-methyl violuric acids, diphenyl violuric acid, *p*-bromphenyloximino-oxazolone,[1]



as well as certain derivatives of nitrophenol, azophenol, pyridine, quinoline and acridine.[2] The salts of the latter will be referred to again later. At present it need only be added that even substances which are similar to ethyl acetoacetate in structure have been observed to exhibit the phenomenon of chromoisomerism.[3]

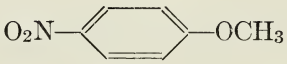
A few illustrations will suffice to bring this matter clearly before the attention of the reader. The freshly precipitated silver salt of violuric acid, for example, is white but if left in contact with its solution, it first changes to an amorphous green and then to a crystalline black-brown compound. If the freshly precipitated colorless salt is filtered and dried, it changes to a dirty rose color, and this change is not due to the action of light. The potassium, rubidium and caesium salts occur in blue and red modifications. If the blue salt is crystallized from hot water a mixture of red and blue salts separates, while if it is subjected to the action of steam it is completely transformed into the red. The latter are stable in perfectly dry condition, but in the presence of moist air revert to the blue. The stability of the different colored salts varies greatly. It is probable that each salt of a definite color has its own

[1] Ber., **42**, 969 (1909).
[2] Ber., **44**, 1783, 3290 (1911).
[3] Ber., **48**, 785 (1915).

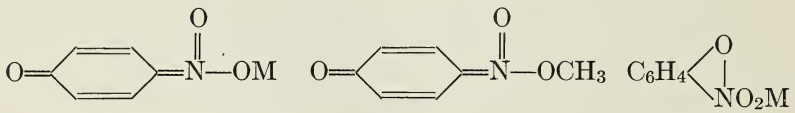
definite sphere of existence outside of which it is metastable or labile. In dry condition and solid form the tendency to isomerization is very slight, but even traces of solvent seem to act catalytically in bringing about rearrangements. It frequently happens that under a given set of conditions one and only one modification of a given salt will be formed. This may isomerize spontaneously into another modification having a different color, but more frequently subsequent changes can be traced to the presence of a minute quantity of some catalyst or to changes in temperature or the nature of the solvent.

Chromotropism is a term used by Hantzsch in referring to variations of color in one and the same salt, and should be distinguished from *variochromism* which is used to express the existence of a given salt in different colored modifications. Silver and potassium salts frequently exhibit the phenomenon of variochromism, illustrations of which have already been noted in the case of violuric acid. For example, Hantzsch has discovered an oximido-ketone which forms colorless, yellow, red, and blue primary salts, each of which represents a distinct and separate modification. These substances by secondary reaction, were also observed to give different colored mixed salts.

Many theories have been advanced to explain the phenomena of chromoisomerism. It has been supposed for example that differences in color could be accounted for on the basis of benzoid-quinoid isomerism. The colorless salts and ethers of nitrophenol were thus assumed to have the formula,



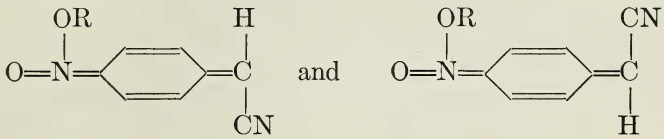
while the corresponding colored derivatives were given one or the other of the following quinoid formulas:



This explanation was soon abandoned since it does not account for the multiplicity of different colored salts which can be obtained from a given acid. These salts seem, moreover, to bear a closer chemical relation to each other than that indicated by the above formulas since they react in all cases to give identical products. That they exhibit slight differences in chemical properties is, however, obvious from the fact that the deeper colored salts react in general much more readily than their lighter colored isomers.

It was then supposed that the different colored salts of a given acid might be polymorphic modifications [1] of one and the same chemical individual. The main objection to such an explanation is to be found in the fact that individual salts having characteristic colors frequently dissolve in organic solvents to form stable solutions and that in so doing they impart their particular colors to their solutions. Molecular weight determinations have, moreover, served to demonstrate that in all cases these salts are present in such solutions in mono-molecular condition and that therefore any explanation of color which is based upon polymorphism is untenable.

Stereoisomerism has been employed by Lifschitz [2] to explain the chromoisomerism of the red and green salts and esters of *p*-nitrobenzyl cyanide to which he gives the formulas:



but this explanation is capable of only a limited application and therefore contributes very little toward the solution of the general problem of chromoisomerism.

The suggestion has also been made that the color of different salts may be due to the action of the solvent since according to Ley it may be assumed that changes in the degree of solution occur during the process of salt formation. For example, the complex which is formed by the union of the solute with one or more molecules of the solvent may alter its composition during the process of neutralization and this change in composition may be accompanied by corresponding changes in color. Such an explanation presupposes a change in the equilibrium relations in the solution as represented by

$$A + nLm \rightleftarrows (A \cdot nLm)$$

$$A \cdot nLm \rightleftarrows (A \cdot nLm) + pLm$$

where A represents the dissolved substances and Lm, the solvent. Experimental evidence does not, however, support this explanation since it has been demonstrated that the solvent frequently plays no part in the process. In fact it is generally conceded that even under the most favored conditions association between the solvent and the

[1] Ber., **43**, 84 (1910).
[2] Ber., **48**, 1730 (1915).

solute plays a very minor part in color changes. The effect of electrolytic dissociation also appears to be negligible.

In order to reach a decision in regard to the constitution of substances of this type A. Hantzsch[1] undertook a systematic investigation of the optical properties of the polychromic alkali salts of oximido ketones dissolved in indifferent solvents. The results of this investigation may be summarized as follows:

I. All polychromic salt solutions contain monomolecular salts (i.e., isomers and not polymers).

II. The color of the solution changes from yellow → orange → red → violet → blue depending upon the positive character of the metal—as indicated by the series Li, Na, K, Rb, Cs, NR_4—and also upon the character of the solvent—as indicated by the series phenol, chloroform, acetic ester, acetone, and finally pyridine.

III. The absorption curves of the weakly colored (yellow) salt solutions indicate that they are very closely related to solutions of the free oximido-ketones (or their acyl and alkyl derivatives). These solutions all show general absorption in the region of the ultraviolet and are in marked contrast to the blue solutions of the more deeply colored salts. The latter show strong selective absorption and resemble the blue solutions of the aliphatic nitroso compounds very closely. They may, therefore, be assumed to contain nitroso-enolic salts.

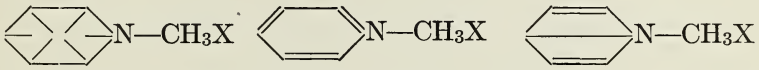
IV. All other colored solutions may be regarded as intermediate between these two extremes since the change in color from blue → violet → red → orange → yellow corresponds to a similar change in the absorption curves of these solutions. Thus the nitroso-band becomes gradually smaller and is shifted more and more in the direction of the ultraviolet until finally in certain yellow solutions it completely disappears. It should be noted that these solutions differ from solutions of the free oximido-ketones and their alkyl and acyl derivatives in that they show a very pronounced absorption band in the ultraviolet, while the latter show either no absorption or very weak absorption in this region of the spectrum.

V. The intermediate colors orange, red, and violet which correspond to intermediate absorption curves may thus actually be regarded as mixed colors, but it must be remembered that in such cases a mixture of blue and yellow produces *red* and not *green*. There are relatively few colorless alkali salts of the true oximido-ketones and where these do exist in solid form they fail to give colorless solutions, being isomerized more or less into salts of the nitroso-enolic type.

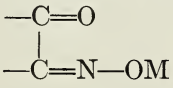
The theoretical deductions which may be drawn from this investi-

[1] Ber., **43**, 82 (1910).

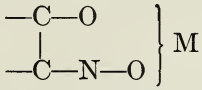
gation seem to Hantzsch to point to the conclusion that changes in color are to be attributed in all cases to changes in constitution. These may be due either to rearrangements of the atoms within the molecule or to rearrangements in the distribution of affinity,[1] in which case the general relations between the atoms remain the same. Phenomena which involve changes in the distribution of affinity without accompanying changes in the relative positions of the atoms in the molecule are referred to as *allodesmism*,[2] and is illustrated by means of the following formulas:



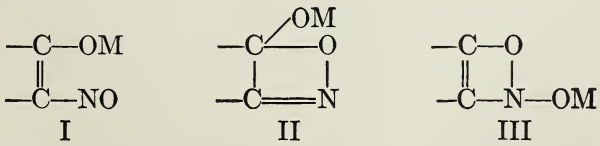
The strongest argument in support of such an explanation of the phenomena under consideration is to be found in the fact that polychromism has never been observed in the case of the simplest oximino salts of the type C=N·OM and thus seems to be conditioned by the presence of both an oxime and a ketone group.



Such compounds resemble the mono- and di-nitrophenols in the fact that they readily tend to undergo intramolecular rearrangements. In the case of the oximido-ketones it may be assumed that in general all varieties of colored salts may be represented by the composite formula:



Such a composite formula may be resolved into individual formulas by simply indicating the particular distribution of affinity in any given case, as for example,



The theory that polychromism is due to differences in the distribution of affinity within the molecule is supported at least in certain

[1] Ber., **44**, 1803 (1911).
[2] Ber., **44**, 1803 (1911).

cases by the fact that the salts in question are chemically identical and it is therefore impossible to explain their relationship on the basis of the usual types of structural and stereo-isomerism. Differences of this character may be regarded in their broader aspects as manifestations of *valency-isomerism*, to which brief consideration must now be given.

The theory of valency-isomerism represents an outgrowth of Werner's theory of partial valencies and was originally advanced to explain the mechanism of certain addition reactions. It has been noted that a number of intensely colored substances are formed as the result of the addition of colorless to weakly colored molecules as, for example, by the addition of amines to quinones and of aromatic bases or hydrocarbons to polynitro bodies. Since in all of these cases the reactions must be considered as simple additions, Werner [1] suspected that they were brought about by the union of residual or partial valencies. Following Hantzsch's investigation of the nitroquinone ethers [2] and polynitrobenzenes [3] and his application of the conception of residual affinities to explain the constitution of these bodies, Werner devoted himself to a comprehensive study of the problem.[4] His conclusions may be summed up by saying that he came to the belief that in general color phenomena of this particular type may be attributed to the saturation of residual valencies. One such valency may with some certainty be allocated to the nitro groups.[5] The position of the other is not certain, but since aliphatic hydrocarbons of the methane series do not form colored addition products with nitrocompounds, it is possible that the presence of free affinity on the unsaturated carbon of the adding molecule forms a second important factor in the reaction.

In the special case of colored salts it is necessary to ascertain the particular rôle which the metal plays in the production of color. This naturally presupposes a study of the conceptions which Werner has developed in regard to the partial valencies of the metals,[6] and also of the applications of these views made by Ley [7] and Tschugaeff. On the basis of such considerations, Hantzsch was at first inclined to believe that residual valencies of the metal were involved in the pro-

[1] Ber., **42**, 4324 (1909).

[2] Ber., **40**, 1570 (1907).

[3] Ber., **41**, 1212 (1908).

[4] Ber., **42**, 4324 (1909); also Werner's "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," p. 241.

[5] Ber., **42**, 4327 (1909).

[6] Ber., **42**, 4327 (1909).

[7] "Farbe und Konstitution bei organischen Verbindungen."

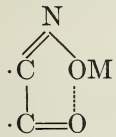
duction of color and that therefore the isomeric chromo-salts possessed the formulas

I
Yellow

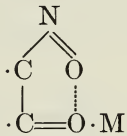
II
Blue

but later he completely abandoned this view.

Such a conception is open to the objection that it presupposes a much greater change in color on ionization than actually is observed. Moreover it also presupposes the presence of residual valencies upon the alkyl groups in the case of the colored ethers of the oximidoketones, and this according to Hantzsch is likewise not in accord with the facts. To avoid such difficulties Hantzsch substituted the following formulas for I and II respectively



Yellow



Blue

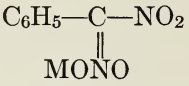
The latter, while still open to objection, seem to explain the relationship better than any formulas at present available. Salts of other colors than yellow or blue may be regarded as mixtures, equal parts of yellow and blue producing red, etc., etc.[1]

The chromoisomerism of nitro-compounds may now be considered somewhat more closely.[2] The phenomenon occurs in connection with the metallic derivatives of a great variety of different compounds. For example, phenyldinitro-methane, which is itself pale yellow in color, in some cases forms salts of the same color while in other cases it forms salts which are either deep yellow or red. A detailed optical investigation of the phenomena seems to indicate that combinations which contain the group NO_2 are present in solutions of free nitro-compounds.

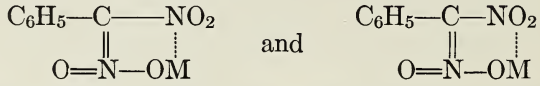
[1] Lifschitz, Ber., **46**, 3233 (1913).
[2] Ber., **40**, 1523 (1907).

Weakly colored salts on the other hand may be assumed to contain the combination

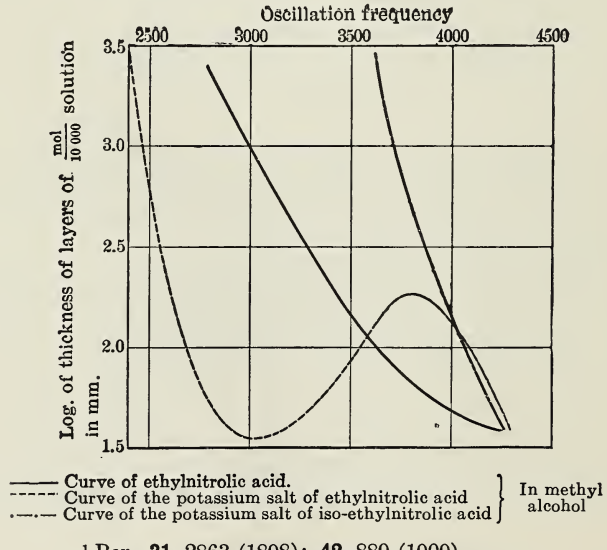
This allows the possibility of stereoisomerism in certain instances as, for example, in the case of the metallic derivatives of phenyldinitromethane



The yellow and red salts may, because of their deeper color, be assumed to possess the partial valency formulas:



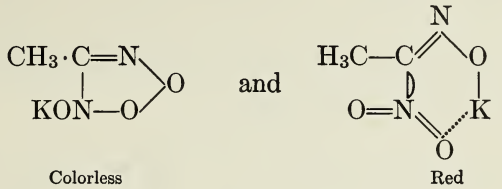
Ethyl nitrolic acid has been very carefully investigated by Hantzsch and O. Graul [1] and has been observed to give two isomeric potassium salts, one red and one colorless. Of these the former is unstable and readily rearranges to give the latter at a temperature of from 45° to 50°. This reaction is not reversible. A spectroscopic investigation of these substances, as represented below,[2]



[1] Ber., **31**, 2863 (1898); **42**, 889 (1909).

[2] Dessertation of G. Kanasirski, Leipzig, 1908.

reveals the very interesting fact that of these three substances the red salt alone possesses selective absorption. While the colorless salt and the free acid may be readily distinguished one from the other, both are characterized by continuous absorption spectra. In this case chromoisomerism may be explained on the basis of the following formulas:



Colorless Red

These formulas are in general agreement with the facts of experiment in so far as it has been demonstrated by Lifschitz that the conductivity of the colorless salt is 15 per cent greater than that of the red salt, and such a difference can be accounted for most readily by supposing that the postassium atom is bound by means of a partial valency in one case and not in the other.

Nitrophenols have also been observed to exhibit the phenomenon of chromoisomerism,[1] and the following types of salts, all of which may be formed by one and the same metal, have been isolated:

1. Colorless (leuco) salts.
2. Colored (chromo) salts.
   (*a*) Yellow.
   (*b*) Red.

Additional facts which seem to contribute to the solution of these and similar questions as to constitution have recently been discovered by Hantzsch who has observed that relatively simple molecules which are similar to ethyl acetoacetate in structure as, for example,

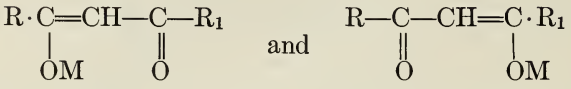
$$R\cdot CO\cdot CH_2\cdot COOR' \quad \text{and} \quad R\cdot CO\cdot CH_2\cdot CO\cdot R'$$

possess the power of combining with colorless metals to give different colored salts. Since the phenomenon is never met with in connection with compounds such as

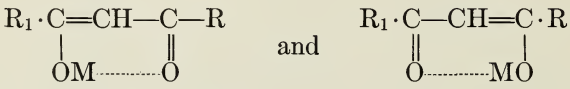
$$RCO\cdot CH_2\cdot COR$$

[1] Ber., **39**, 1073, 1084 (1906); **42**, 2119 (1909); **43**, 3049, 3366 (1910); **44**, 1771 (1911); **45**, 85 (1912); also Lifschitz, "Änderungen der Lichtabsorption bei der Salzbestimmung," pp. 55, 73.

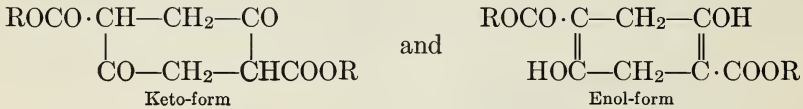
in which the two residues are identical, it would seem to be conditioned by the unsymmetrical structure of the molecule and may therefore be expressed in terms of the formulas



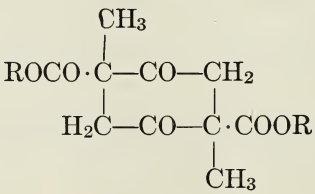
Here again partial valencies may be supposed to function in a manner which involves ring formation,[1] viz.,



Isomerism of this type has not been observed in connection with ethyl acetoacetate itself but very interesting discoveries have recently been made in the case of an ester of succinyl succinic acid. The structure of this substance has been the subject of much debate and arguments have been advanced for and against the following formulas

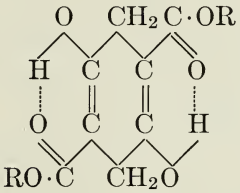


Hantzsch is now of the opinion that the chemical and optical relationships of the substance are correctly expressed by means of the *enol* formula, since the substance readily adds bromine to give a tetrabromide and since its absorption spectrum is radically different from that of *c*-dimethylsuccinylsuccinic ester

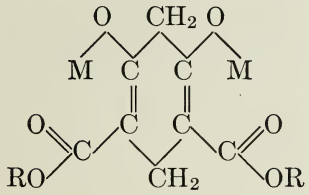


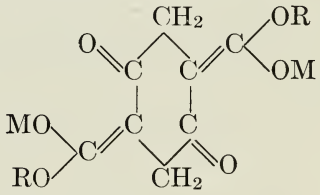
[1] Ber., **43**, 3052 (1910); **45**, 85 (1912); **48**, 785, 800, 1407 (1915); also Gibbs and Brill, Chem. Centralbl., **1915**, II, 392; Philippine Jour. Sci., **10A**, 51 (1915); Liebermann, Annalen der Chemie, **404**, 272 (1914); H. Kauffmann, Ber., **48**, 1269 (1915); H. Pauly, Ber., **48**, 934, 2010 (1915); Hantzsch, Ber., **48**, 1332 (1915).

The stability of the *enol* modification is evident from the fact that the absorption curve of the substance is almost the same in all solvents. This would seem to indicate that but one modification is present in solution instead of equilibrium mixtures of the two forms such as are observed, for example, in the case of ethyl acetoacetate. According to Hantzsch this remarkable stability of the *enol*-form may be accounted for by supposing that the free affinity of the carbonyl oxygen atom is saturated in such a manner as to produce the effect of ring formation, viz.,



The chromoisomerism of the yellow and red salts which are derived from this acid is interpreted by means of the following formulas:





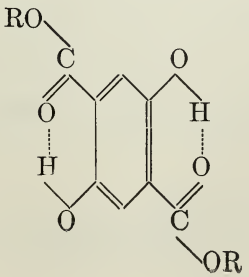
Succinylsuccinic ester oxidizes to give dioxyterephthalic ester

$$C_6H_2(OH)_2(COOR)_2$$

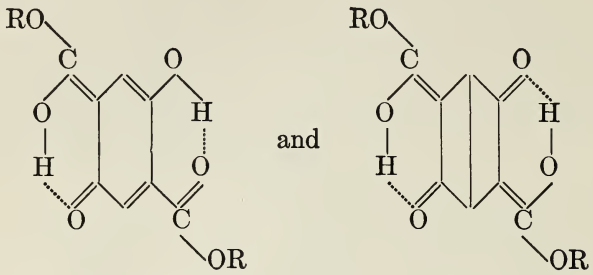
which exists in two isomeric modifications. Of these one is colorless and labile and has an absorption spectrum which is practically identical with that of the corresponding dimethyl ether

$$C_6H_2(OCH_3)_2(COOR)_2$$

so that it may reasonably be assumed to possess a benzoid configuration, i.e.,



The second modification, on the other hand, is yellow in color, stable, and shows a quite different absorption. It may be assumed to possess one or the other of the following quinoid structures:



Mono-quinoid Di-quinoid

Of these formulas the first seems best fitted to the facts since the diagonal linkage which is represented as present in the second, has not as yet been shown to occur under similar conditions. Both the colorless and the yellow modifications react to give salts which are respectively yellow and red and for which corresponding configurations may be assumed.

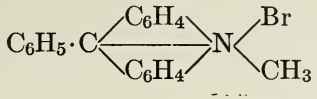
Chromoisomerism in the pyridine, quinoline, and acridine series has already been referred to and the statement was then made that the phenomena are similar to that which has been described in the case of the oximido-ketones. Here again molecular structure and stereoisomerism alone seem to afford no adequate explanation for the relationships which have been observed to exist among the different colored isomers and these must therefore be interpreted as due to differences in the distribution of valencies within the unsaturated chromophore.[1] Since the relationships are somewhat complicated the subject must be considered in some detail.

It has been known for a long time that certain pyridine, quinoline and acridine salts, $C_5H_5N \cdot HX$ and $C_{10}H_7N \cdot HX$, etc.,—exist in different colored modifications.[2] This is conspicuously true of the alkyl iodides, as for example $C_5H_5N \cdot CH_3I$, $C_{10}H_7N \cdot CH_3I$, etc. In the pyridine series these substances are either colorless or yellow, in the quinoline series almost colorless or dark yellow to deep orange, while in the acridine series the variations in color are still more marked.

[1] Ber., **44**, 1783, 1801–1803 (1911).

[2] Claus and Decker, Jour. prakt. Chemie, **39**, 305 (1889); Decker, Ber., **37**, 2939 (1904); Jour. prakt. Chemie, **79**, 342 (1909).

Hantzsch [1] has, for example, recently discovered polychromic salts of N-phenyl- and N-methyl-phenylacridinium halides,



with colorless anions which can be obtained in almost every variety of color.

In the case of these substances polychromism is exhibited both by the solid salts and their solutions and has been made the subject of very thorough optical investigation by Hantzsch and Schuler.[2] Their results seem to indicate "that all acridinium salts, whether in solid form or in solution, consist of equilibrium mixtures of three simple types, namely yellow, green and red,—although at times certain conditions may favor the independent existence of one to the exclusion of the other two."

Hantzsch is of the opinion that the isomerism of these different ammonium salts is conditioned by the fact that one of the four atoms or groups in union with nitrogen is less securely bound than the other three. If this conception is expressed in terms of Werner's theory, according to which salts of this type may be formulated as

$$H_3N\_\_H—Cl$$

it follows that the labile atom or group is the one in union with the acid radical.

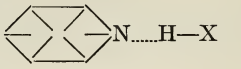
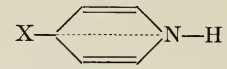
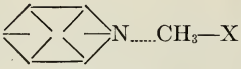
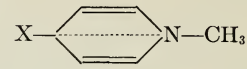
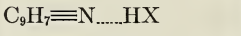
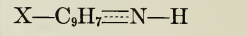
It will be recalled that according to Werner's theory two isomeric modifications are theoretically possible in the case of all quaternary ammonium salts in which one of the four residues is different from the other three, viz.

$$RRRN\_\_R_1—X \quad \text{and} \quad RRR_1N\_\_R—X$$

In cases where either the radical R or R_1 is capable of tautomeric rearrangement, as, for example, benzoid $\rightleftarrows$ quinoid, the number of isomeric modifications will obviously be increased.

Following a line of argument which is based more or less upon probabilities, Hantzsch has formulated these relationships in the following manner:[3]

[1] Ber., **42**, 68 (1909).
[2] Ber., **44**, 1799 (1911).
[3] Ber., **44**, 1805 (1911).

	Benzoid, Colorless, Optically Normal	Quinoid, Yellow, Optically Abnormal
Pyridonium salt, $C_5H_5N \cdot HX$		 Only stable solution of the iodide
Alkylpyridonium salt, $C_5H_5N \cdot CH_3X$	 Stable form	 Only stable as iodide in chloroform solution
Quinoline and Isoquinoline salts		

All other colored modifications must be regarded as mixed salts. From the ease with which the two groups of salts isomerize Hantzsch deduced certain rules according to which a particular salt may be recognized as belonging to one or the other class:[1] " the so-called benzoid salts are characterized by the presence of a stable pyridine ring which like the true benzene ring possesses very little free affinity. The absorption spectra resemble that of pyridine. The so-called quinoid salts, on the other hand, are characterized by the presence of an unstable acridine ring and possess a relatively great amount of free affinity. They do not, however, resemble acridine in their absorption, being much more deeply colored and showing a much stronger selective absorption."

It must be emphasized that all such attempts to explain these phenomena are more or less premature, since the whole question is in a state of flux at the present time and ideas as to the best mode of representing these relationships have not yet become settled.[2] Kauffmann's particular interpretation is given in the " Valenzlehre," p. 512.

Still another type of isomerism has been described by Hantzsch under the title of *homochromisomerism*.[3] While chromisomers have the same chemical properties but differ optically as to their color and absorption, homochromisomers are almost identical in all of these respects and also possess the same molecular extinctions and refractions. Such modifications can be distinguished only by differences in their melting points, solubilities, etc. Since in solution they show the same

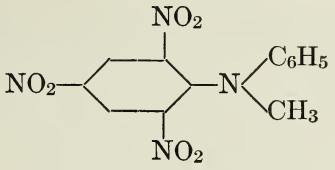
[1] Ber., **44**, 1783, 1809 (1911); **49**, 1865, 2169 (1916).

[2] Compare Kehrmann, Ber., **49**, 1338 (1916); **50**, 24 (1917); also **50**, 1204 (1917).

[3] Ber., **43**, 1651 (1910).

molecular weight and are recovered unchanged, they must be regarded as isomeric and not polymeric forms.

Examples of homochromisomerism are to be found in the stereoisomeric quinonoximes, nitranilines and possibly also among the colored salts of the dinitro-compounds. Methylphenyl picramide,



affords perhaps one of the best illustrations of this phenomenon. This substance is formed by the action of methylaniline upon picryl chloride and appears as either a low melting (α) or a high melting (β) modification, depending upon whether benzene or alcohol respectively is used as the diluent in the reaction. The α form melts at 108° and crystallizes from methyl alcohol, acetic acid, ether, chloroform, carbon bisulphide and pyridine in the form of dark red prisms. The β modification possesses the same color, melts at 128 to 129°, and crystallizes unchanged from benzene, pyridine and carbon bisulphide. Both forms are monomolecular. The α modification is readily transformed into the β without suffering any change in weight, upon heating at 100° and also upon recrystallization from benzene. The high-melting isomer, on the other hand, rearranges to give the α form without change in weight at ordinary temperatures, and also upon recrystallization from acetone [1] alcohol, ether, chloroform and carbon tetrachloride.

Both isomers give the same ultraviolet absorption spectra. Their molecular extinctions are identical within the limits of experimental error and their molecular refractions show only slight differences. Biilmann,[2] who has verified the majority of Hantzsch's experimental results, discovered the additional fact that when melted each of these substances can be made to isomerize into the other upon seeding. This observation led him to the conclusion that they represent polymeric modifications and not a new kind of isomerism. Hantzsch,[3] however, continues of the opinion that such is not the case. No satisfactory explanation of homochromisomerism has as yet been found.

The number of isomers which have been discovered in the case of

[1] Ber., **44**, 835 (1911).

[2] Ber., **44**, 834; Ber., **43**, 1651; Ber., **44**, 3153 (1911); also Hantzsch, Ber., **44**, 2001 (1911).

[3] Ber., **44**, 2007 (1911).

this and other classes of substances, cannot be accounted for on the basis of the old structural or stereo-formulas. This becomes even more apparent if the following facts are considered. H. Stobbe [1] has discovered that *m*-nitrobenzaldesoxylbenzoin

$$NO_2 \cdot C_6H_4 \cdot CH{=}C(C_6H_5) \cdot COC_6H_5$$

exists in three isomeric forms all of which are yellow in color and monomolecular in composition. If these isomers are represented respectively by *A*, *B* and *C* it may be said that *A* has the lowest melting-point and that its properties are essentially different from *B* and *C*. Thus although it gives the same chemical derivatives as *B* and *C*, it reacts much more readily and the absorption spectra of its solutions are different from those of *B* and *C*. In short all of the chemical and physical properties of the substance indicate that it is a chemical isomer of *B* and that the relationship is in all probability correctly represented by means of the following formulas:

$$\begin{array}{c} NO_2 \cdot C_6H_4 \cdot CH \\ \| \\ C_6H_5 \cdot C \cdot COC_6H_5 \\ A \end{array} \qquad \text{and} \qquad \begin{array}{c} NO_2C_6H_4 \cdot CH \\ \| \\ C_6H_5CO \cdot CC_6H_5 \\ B \text{ and } C \end{array}$$

The difference between *B* and *C* is much less pronounced and may be explained by supposing either that the two substances are closely related chemical isomers or that they are dimorphic. In the former case it may be assumed that the differences are due to differences in the degree of saturation of the affinity of their respective atoms and that the relationship is such that a given molecule can pass from one condition to the other upon solution, melting, seeding, etc. In the second case the atomic relationship within the two molecules *A* and *B* may be supposed to be identical and the observed differences in the properties of the two substances must be accounted for on the basis of differences in the arrangements of the molecules, accompanied by differences in crystalline form.

In order to decide this question in one way or the other it is obviously necessary to know whether the two different crystalline individuals lose their identity when dissolved, or melted, or when in the gaseous state, for if their solutions possess the same absorptions, refractions, viscosity, etc., the substances in question must of necessity be physically and chemically identical. Experiment shows that while both *B* and *C* dissolve to give solutions which ultimately become identical in all respects, such solutions nevertheless exhibit perfectly definite although slight

[1] Annalen der Chemie, **374**, 260 (1910); Ber., **44**, 1481 (1911).

differences if examined immediately after solution of the substance has taken place. Stobbe, therefore, concludes that *B* and *C* actually represent different chemical individuals but that upon solution or melting they pass instantly into equilibrium mixtures. Many similar phenomena have been observed. For example, Pfeiffer describes yellow and orange-colored modifications of this class of compounds which are stable at low and high temperatures respectively. The yellow form dissolves in acetic acid to give a yellow solution, which if heated above 100° gradually changes to an orange color and on cooling precipitates the isomeric orange colored modification. Both forms dissolve in any given solvent to give solutions which are identical but the color varies in the case of different solvents. For example, benzene solutions are almost colorless, while alcohol and acetic acid solutions have a somewhat deeper color and trichloracetic acid solutions, a very deep color. In general, the variation is from straw color to yellow to orange.

The property of forming yellow or orange solutions depending upon the temperature must be regarded as a characteristic which is common to all unsaturated aromatic compounds but which may be intensified by the bathochromic effect of substituents such as the methoxy groups. The nitro-methoxystilbenes, for example, resemble the unsaturated ketones in their ability to form addition products with acids and metallic salts. Thus Pfeiffer [1] and his students have obtained an orange colored compound having the formula

$$[NC \cdot C_6H_3(NO_2) \cdot CH{=}CH \cdot C_6H_4OCH_3]_2SnCl_4$$

by the action of stannic chloride upon the yellow modification of 4-cyan-2 nitro-4 methoxystilbene. This product on decomposing regenerates the original yellow modification of the parent substance. On the other hand 4-cyan- 2-nitro-4-methoxystilbene dissolves in benzene to give a yellow solution from which a yellow addition product

$$[NC \cdot C_6H_3(NO_2) \cdot CH{=}CH \cdot C_6H_4OCH_3]_2C_6H_6$$

separates. The latter decomposes to give a free stilbene which is orange in color and which appears to represent a second distinct modification. In an analogous manner benzoylaminonitromethoxystilbene combines with acetic acid to give an addition product which is yellow, and with trichloracetic acid to give an orange colored compound. Both substances decompose to give respectively orange and yellow modifications

[1] Ber., **48**, 1777 (1915).

of the free stilbene. It is rather remarkable that the yellow addition product gives a yellow modification of the parent substance, but this may be explained by supposing that both modifications of the free stilbene coexist in a condition of dynamic equilibrium in solution and that the preponderance of one or the other form depends upon specific conditions. If this assumption is correct yellow solutions might be expected to contain the yellow modification while as a matter of fact it has been observed that yellow benzene solutions give the orange and not the yellow form of 4-cyan-2 nitro-4-methoxy stilbene.

The latter observation led Pfeiffer to assume that the phenomena could not be explained on the basis of normal isomerism and that the two modifications must, therefore, be regarded as polymorphic rather than as isomeric forms. Differences in color may be explained on the basis of halochromism if different molecular compounds are assumed to possess varying amounts of free affinity. In the case of different colored addition products this conception may be expressed by means of the general formulas

$$\underset{\downarrow}{RNO_2}\cdots\cdots SnCl_4, \qquad \underset{\downarrow}{R\cdot NO_2}\cdots\cdots HOCO\cdot CCl_3$$

where the arrow serves to locate the position of the free affinity present in the molecule but does not in any way define the variations in quantity upon which a lightening or a deepening of color depends.

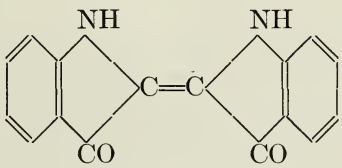
Differences both in the color and in the crystalline structure of different polymorphic modifications of one and the same chemical individual may be explained simply by extending this conception to the higher orders of molecular compounds.[1] If, as von Laue, W. L. and W. H. Bragg suppose, crystals may be regarded as complex molecular compounds,[2] difference in crystalline structure in the case of one and the same chemical individual must be due to differences in the way in which the molecules are combined. Assuming that combination takes place according to the rules embodied in Werner's doctrine of coordinate relationships among atoms, it is easy to see how one such complex might differ from another in the relative concentration of free affinity in definite positions. The association of molecules might, for example, result from the union of either principle or partial valencies. Thus two molecules of nitromethoxystilbene might combine by the mutual saturation of two ethylene groups. In this case the associated molecules would probably be lighter than the unassociated molecules

[1] Pfeiffer, Ber., **48**, 1777 (1915).

[2] Zeitschr. anorg. Chemie, **92**, 376 (1915).

since reactions of this type are usually accompanied by increased saturation or in other words by a decrease in the free affinity of the substance. Another and very different condition might result from the saturation of partial valencies present on different groups. For example, nitromethyoxystilbene, $O_2NC_6H_4 \cdot CH{=}CH \cdot C_6H_4OCH_3$, may be regarded both as a nitro-compound and as a phenol ether and since it is known that these two classes of atomic groupings interact by the saturation of their partial valencies, it may be assumed that nitromethyoxystilbene molecules are capable of reacting in the same way. Associated molecules of this type would be coordinately bound by the saturation of partial valencies on the nitro-groups and unsaturated carbon atoms respectively and, because of an increase in the free affinity of the nitrogen, should possess a deeper color than the unassociated molecules. The relative depth of color would vary with the relative amount of free affinity in any given case. Whatever the merits or demerits of this conception it at least serves to elucidate the relationships which exist between true chemical isomers on the one hand and polymorphic modifications on the other.

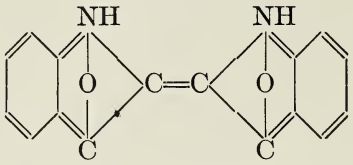
The more recent theories in regard to the relation between color and chemical constitution may be applied in the elucidation of certain phenomena which have been observed in connection with the chemistry of dyes of the indigo group and also of the so-called mordant dyes. According to the formula which was originally brought forward by Baeyer to explain the chemical constitution of indigo



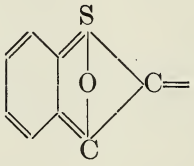
the color of the substance may be accounted for by supposing that the two conjugated systems CO—C=C—CO act as chromophores, each being reinforced respectively by an NH group which functions as an auxochrome. This formula does not, however, serve to explain the color of indigo in terms of the more recent conception in regard to the relation between color and constitution so that it has now been superseded by another expression which was first suggested by M. Claass [1] and which has been made the basis for new theoretical developments. Claass made the important observation that the characteristic deep blue color of indigo is not affected by the substitution of the group SO

[1] Ber., **49**, 2079 (1916).

for the group CO. This discovery was rather remarkable in view of the fact that sulphoxyl has not been found to act as a chromophore in other of its combinations and the presence of the ethylene group, C=C, is not in itself sufficient to account for the deep color of the compound. In order to explain the phenomenon Claass was led to assume that in the case of indigo and its sulphoxyl derivative the color is conditioned by two factors (*a*) the formation of an inner salt by the interaction of the NH group with either of the acidyl groups, CO or SO, and (*b*) the presence of an *ortho*-quinoid complex, viz.,



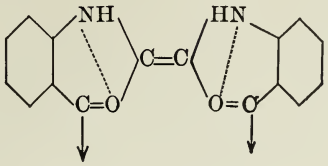
The chromophore in thioindigo was assumed to possess an analogous structure, the only difference being the replacement of the NH group by sulphur:



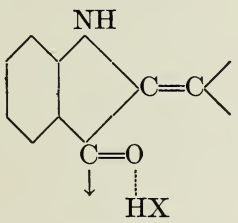
J. Lifschitz and A. Lourié [1] then made the discovery that the absorption spectrum of indigo is distinctly different from that of substances which are known to possess a quinoid structure. In fact the type of absorption which was found to be characteristic of dyes of the indigo group bore a striking resemblance to the absorption of the halochrome derivatives of the ketones. The optical properties of these two classes of compounds are, moreover, in striking agreement with their chemical properties as is illustrated, for example, by the behavior of indigo, thioindigo, etc., toward sulphuric acid. Thus both investigators found that the change suffered by the spectrum of indigo under the action of sulphuric acid resembled in type that suffered by halochrome ketones under the action of the same reagent. These facts seemed to indicate that some modification of the Claass' formula for indigo was desirable and Lifschitz and Lourié, therefore, brought forward a new formula which avoided the assumption of quinoid structure and attempted to

[1] Ber., **50**, 897 (1917).

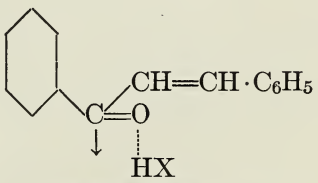
explain the phenomenon of color in terms of Pfeiffer's theory of halochromism, viz.,



According to this conception the similarity in the behavior of indigo and halochrome ketones in the presence of sulphuric acid and other reagents may be accounted for on the basis of the following formulas:



Indigo



Benzal acetophenone

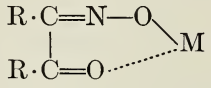
Another important group of organic dyes consist of substances which like alizarine react with the oxides of certain metals as, for example Al, Fe, Cr, Cu, Sn, Co, etc., to form colored insoluble salt-like compounds known as color lakes. Substances of this type are usually applied to fabric which has first been mordanted or which, in other words, has first been treated with a salt of the particular metal that is known to give the desired color. Under these circumstances the color lake is usually deposited in a very stable form upon the fabric. A careful investigation of the different classes of substances which possess the power of reacting with metallic oxides to form lakes led to the discovery that this property is conditioned by certain definite configurations of the molecule. For example, the only oxyanthraquinones capable of forming lakes are those which, like alizarine, contain two hydroxyl groups in the *ortho* positions.[1] Later R. Möhlau and F. Steimmig[2] observed that monohydroxyl derivatives of aromatic hydrocarbons in general possess the power of forming lakes provided only that the hydroxyl group occupies an *ortho-* or *peri*-position with reference to the chromophore CO. Previous to this time Kostanecki[3]

[1] Rule of Lievermann and St. von Kostanecki, Annalen der Chemie, **240**, 245 (1887).

[2] Zeitschr. f. Farbens u. Textilchemie, **3**, 358 (1904).

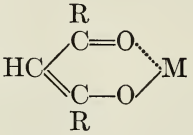
[3] Ber., **20**, 3146 (1887); **22**, 1347 (1889).

had pointed out that substances with certain isonitroso and other atomic groups in analogous positions with reference to ketone groups, are able to form color lakes. Examples of this kind continued to multiply but it was not until 1907 that L. Tschugaeff [1] called attention to the fact that in the case of the isonitrosoketones the power to form color lakes depends upon the ability of the substance to enter into inner cyclic salt-like combinations such as for example,

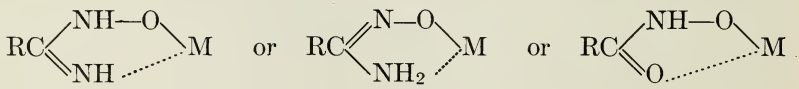


According to this conception lakes are to be regarded as complex compounds of cyclic structure, the stability of which depends in part at least upon the presence of a five membered ring in the molecule.

In order to test the accuracy of this theory A. Werner [2] investigated a large number of organic compounds which possess the power to form so-called inner complex salts of the general formula:



Salts of this type are distinguished by the fact that the metallic atom is simultaneously bound by a partial and by a principal valence and that ring formation depends upon an intramolecular saturation of partial valencies. The results of Werner's investigation showed that such relatively simple substances as benzoyl acetone, dibenzoyl methane, anisoyl benzoyl methane and others are capable of forming inner complex salts which belong to the class of color lakes. P. Pfeiffer [3] pointed out, moreover, that oxy-ketones and oxy-quinones in general possess this property as do also amido-oximes and hydroxamic acids. In the latter case the inner complex salts belong to the same general class of mordant dyes and may be assumed to possess formulas corresponding to



These observations led Werner to formulate his "theory of mordants" according to which "substances which react with mordants to

[1] Jour. prakt. Chemie, **76**, 88 (1907).

[2] Ber., **41**, 1062 (1908); also "Neuere Anschauungen, etc.," 3rd Ed., p. 247.

[3] Ber., **44**, 2653 (1911); Annalen der Chemie, **398**, 138 (1913).

give dyes must be so constituted as to contain (1) a salt forming group and (2) a second group which is capable of entering into coordinative union with a metallic atom. These two groups must be so placed with reference to each other that inner complex metallic salts may arise." This characterization has been found to be in general agreement with all the facts that have been discovered up to the present time.[1] In conclusion it may be noted that the number of substances falling within this category of dyes has been increased by the recent discovery of R. Möhlau [2] who has found that certain complicated monoatomic phenols, as for example α- and β-anthrols, and also certain multiatomic phenols of both simple and complex structure possess the ability to form mordant dyes.

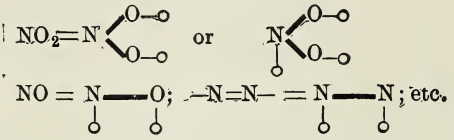
Absorption phenomena have been accounted for by J. Stark on the basis of purely physical considerations and in conclusion these may now be considered briefly. Investigations in the fields of the cathode rays and radioactivity have led to the formulation of the hypothesis that chemical atoms are compounded exclusively of positive and negative units of electricity. Stark assumes that extended positively charged areas exist on the surfaces of the atoms and that above these and in definite positions in relation to them are point-like negative electrons. The latter are supposed to play the part which has commonly been assigned to valency and to bring about the union of two or more atoms. They may, therefore, be referred to as *valence-electrons*. From the standpoint of the optical relationships of chemical compounds valence-electrons may be differentiated into three classes, namely, unsaturated, saturated and semi-detached ("gelockert"). For example, if an electron is attached only to its own and to another atom, it is unsaturated; and if for any reason the attraction by which it is held to the positive sphere of its own atom is weakened so that it becomes more or less free to change its position or even to become detached, it is said to be semi-detached or labile. The latter condition is brought about by the combination of a given atom with other atoms, and is possible only in the case of multivalent atoms.

Stark assumes that valence-electrons are the centers of the emission and absorption of light in band spectra and that the semi-detached or labile electrons play a particularly important part in connection with these phenomena. According to this theory the kinetic energy involved in the recurrent separation and union, which takes place between an electron and the positive sphere of its atom, is transformed into the

[1] Compare R. Scholl, Ber., **51**, 1420 (1918); **52**, 565 (1919); also O. Baudisch, Ber., **51**, 1058 (1918).

[2] Ber., **52**, 1730 (1919).

radiant energy of light. According to calculations, which cannot be inserted here but which will be referred to again later, absorption in the impenetrable ultraviolet and in the infra-red is due to the presence of unsaturated and saturated valence electrons respectively. The semi-detached electrons, on the other hand, are responsible for band spectra which lie beyond 0.0007 mm. For example, benzene possesses electrons of this type and their presence in the following chromophores is indicated by means of the small circle



It is supposed that the relative degree of detachment of such electrons varies and that it is influenced, for example, by the substitution of the above groups in the benzene rings, or by the combination of several chromophores. In the cases where the lability of the electrons is increased the absorption bands of the substance may be observed to shift in the direction of the red. It is obvious that in this way the old idea of chromophores may be combined with the more modern conceptions of the *electron theory* [1] in interpreting absorption phenomena.

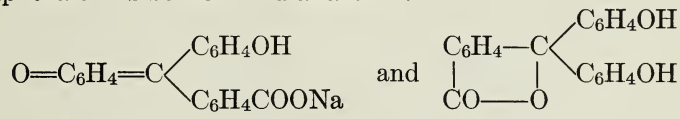
[1] Compare H. Ley, "Farbe und Konstitution," p. 68.

CHAPTER XVII

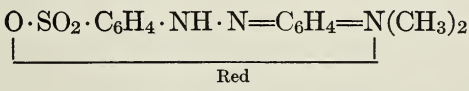
THE THEORY OF INDICATORS

At the time of the development of the ionic theory Ostwald [1] undertook an investigation in regard to the color of ions the results of which led him to suppose that ions possess definite and characteristic absorptions and upon this assumption he proceeded to develop a new theory of indicators.[2] According to this theory indicators are colorless substances belonging either to the class of weak acids or weak bases, which readily dissociate to give colored ions. Phenolphthalein, for example, dissociates to give an ion having an intensely red color although its undissociated molecule is colorless. The color of the ion thus becomes apparent whenever a highly dissociated salt is formed from the acid which is itself practically undissociated.

Later Stieglitz [3] expressed the opinion that color changes in indicators are due not to the phenomenon of dissociation, but to intramolecular rearrangements. According to this view the sodium salt of phenolphthalein is assumed to have a quinoid structure while free phenolphthalein is benzoid and a lactone:

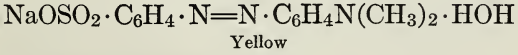


Red solutions of the free acid of methyl orange are accounted for in an analogous manner and are supposed to contain molecules having quinoid structure because, as compared with their alkaline solutions, they possess relatively deep colorations:



Red

and



Yellow

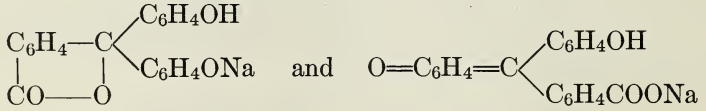
[1] Zeitschr. physikal. Chemie, **9**, 579 (1892).

[2] "Die wissenschaftlichen Grundlagen der analytischen Chemie," 1894, p. 104.

[3] Jour. Am. Chem. Soc., **25**, 1112 (1903); also Kremann, Zeitschr. anorg. Chemie, **33**, 87 (1903); Bredig, ibid., **34**, 202 (1903), and Veley, Zeitschr. physikal. Chemie, **57**, 148 (1907).

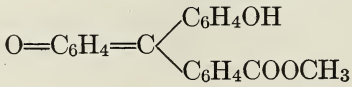
Hantzsch had previously expressed views similar to those of Stieglitz and after laying the foundation of his theory of chromoisomerism he again returned to the problem. Realizing that his assumption that "every appearance of color developed during the process of salt formation with colorless metallic ions is due to intramolecular rearrangements," was capable of experimental demonstration in the case of indicators, Hantzsch undertook a critical examination of the subject. The theory that ionization phenomena might in themselves be sufficient to account for changes in color seemed to him most improbable from a chemical point of view: (1) Because all colorless acids and salts whose constitutions are unalterable form colorless ions. The only true acids which give colored ions are those which in undissociated condition are themselves colored. From this it follows that color is independent of the presence or absence of ions. (2) Because numerous colorless compounds such as dinitroethane, nitroform, violuric acid, etc., which form colored ions, have been shown to be pseudoacids or substances in which intramolecular rearrangements always precede neutralization reactions.[1] These facts taken together seem to indicate that in the case of indicators changes in color depend unconditionally upon changes in constitution and that the formation of ions therefore represents a secondary process, the ions being colored only because the undissociated molecules from which they are formed are also colored. The salts of phenolphthalein are in fact colored in the solid, that is to say in the undissociated condition.

Hantzsch supposes, in other words, that indicators belong to the class of tautomeric substances. If this is so it should be possible to demonstrate that phenolphthalein, for example, is actually capable of forming two series of salts, one colorless and the other colored, corresponding respectively to the lactoid and quinoid formulas:



All attempts to do this have been unsuccessful up to the present time. Two isomeric series of ethers and esters having the required properties have, however, recently been discovered.

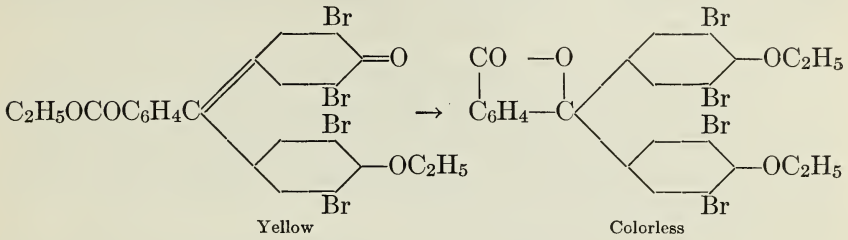
In 1906 Green and King[2] prepared a colored methyl ester from colorless phenolphthalein to which they gave the formula:



[1] Ber., **39**, 1090 (1906).

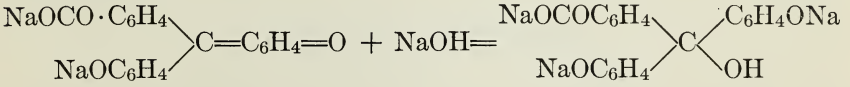
[2] Ber., **39**, 2365 (1906).

but the actual existence of such a substance was doubted by H. Meyer [1] until Hantzsch and K. H. Meyer [2] verified these results. Later R. Meyer and Marx [3] obtained an intensely yellow diethyl ester by treating the silver salt of tetrabrom-phenolphthalein with methyl iodide according to the method of Hantzsch and Gorke. This substance readily rearranges to give a colorless isomer:



These investigators [4] were able to show later that analogous esters could be prepared from phenolphthalein itself, and that again in this case the labile quinoid modification was yellow and rearranged in the process of crystallization to give the colorless, stable, lactoid form.

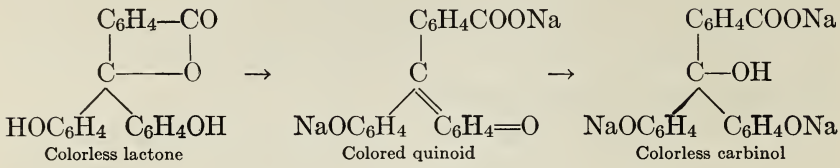
The tautomeric character of phenolphthalein has thus been clearly demonstrated and as a result the theory of rearrangement has been placed upon a sound experimental basis. The mechanism of the change from a red to a colorless solution by the action of an excess of concentrated alkali has, however, not as yet been satisfactorily accounted for. Hantzsch and K. H. Meyer have suggested a possible solution of this problem. The bleaching of phenolphthalein solutions by the cation of concentrated alkali is not instantaneous as has been shown by means of conductivity measurements. These investigators, therefore, argue that it is probably accompanied by rearrangements in the molecule in he sense of



This would explain the end changes in reactions where phenolphthalein is used as an indicator. To recapitulate, free phenolphthalein is a lactone which first isomerizes in alkaline solution and then reacts to give a quinoid salt having a red color and capable of electrolytic dis-

[1] Ber., **40**, 2431 (1907).
[2] Ber., **40**, 3480 (1907).
[3] Ber., **40**, 1437 (1907).
[4] Ber., **40**, 3603 (1907).

sociation into colored ions. In the presence of an excess of alkali this salt hydrolyzes to give a derivative of triphenyl carbinol:



Vorländer had already pointed out that the ionic *theory of indicators* was unable to account for the changes in color observed in the case of derivatives of aminoazobenzene.[1] If, for example, the intense violet red color of acid solutions of aminoazobenzene depends wholly upon the formation of colored ions such as

$$C_6H_5 \cdot N{=}N \cdot C_6H_4NH'_3$$

it follows that its trimethyl derivatives should also give intensely colored ions, viz.,

$$C_6H_5 \cdot N{=}N \cdot C_6H_4N(CH_3)'_3$$

but as a matter of fact this salt dissociates to give ions which are of almost the same color as azobenzene itself. It would, therefore, seem that color cannot in this case be conditioned solely by ionization.

Hantzsch [2] has discovered recently that the salts of aminoazobenzene exist in two series which are sharply differentiated from each other but which are nevertheless readily transformed one into the other:

1. True azo salts of orange color with spectra similar to azobenzene:

$$C_6H_5 \cdot N{=}N \cdot C_6H_4NR_2HX$$

2. Quinoid salts of violet color with characteristic quinoid band spectra

$$C_6H_5 \cdot NH \cdot N \cdot C_6H_4 \cdot NR_2X$$

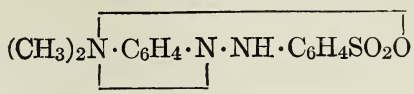
This discovery seemed to solve the problem of color changes in the case of methyl orange (helianthine). The orange-colored solutions of this indicator were assumed to represent solutions of true azo salts,

$$(CH_3)_2N \cdot C_6H_4N{=}NC_6H_4SO_3Na$$

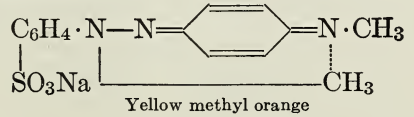
[1] Ber., **36**, 1485 (1903); Annalen der Chemie, **320**, 116 (1902).

[2] Ber. der Chem. Ztg. über Naturforscherversammlung in Dresden, 1907, p. 59; Ber., **41**, 1187 (1908).

while the free violet coloring matter was supposed to consist of an inner quinoid salt,

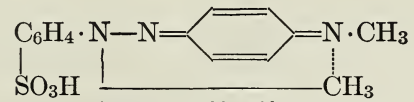


This interpretation of the phenomena has, however, been modified by Hantzsch [1] as the result of a careful study of the absorption spectra of these substances. Investigations along this line show that the yellow modification of helianthine is not azoid but quinoid in character and that its structure is almost identical with that of the red modification. The change from the yellow to red cannot therefore be construed as representing a rearrangement from a yellow azoid to a red quinoid salt but must be regarded as a rearrangement of one quinoid valence isomer into another. In other words the yellow and red modifications of helianthine are not structural but chromo-isomers and the change from one into the other must be formulated in terms of partial valency formulas. For example alkaline solutions of methyl orange may be supposed to contain the salt



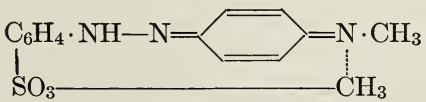
Yellow methyl orange

The addition of acid to such a solution first sets free the corresponding acid,



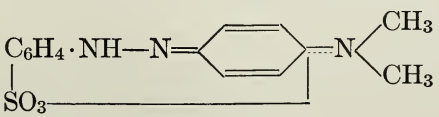
Yellow unstable acid

but this rearranges immediately to give the yellow modification of helianthine which may be regarded as an inner complex salt having the formula



Yellow helianthine

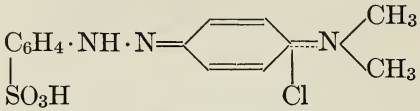
The latter then isomerizes to give the red modification



Red helianthine

[1] Ber., **46**, 1537 (1913); **48**, 158 (1915)

and this in the presence of an excess of acid passes into a red acid salt, which in the case of hydrochloric acid possesses the following formula:



Red hydrochloride

These formulas if correct fully account for the color changes which accompany neutralization phenomena in the presence of methyl orange as an indicator. It will be noted that the change from yellow to red depends upon an isomerization equilibrium of the type

$$\text{yellow helianthine} \rightleftarrows \text{red helianthine}$$

The appearance of the red modification depends upon the presence of free hydrogen ions and its formation is favored by an increase in the concentration of these ions. It does not follow, however, that the appearance of the yellow isomer depends in the same way upon the presence of alkali, since at present it can only be said that while the red isomer is stable in the presence of hydrogen ions the yellow modification is stable in the absence of these ions. The fact that the addition of alkali often leads to the formation of the yellow isomer may, according to Hantzsch, be explained by supposing that under such circumstances the alkali functions merely to remove the hydrogen ions which are present in the solution. Helianthine when dissolved in absolute alcohol remains yellow even after acetic acid has been added because in the complete absence of all moisture no hydrogen ions are formed. This shows how important it is to titrate in aqueous rather than in alcoholic solutions when methyl orange is used as an indicator in neutralization reactions.

W. Ostwald [1] has recently suggested that changes in color in the case of indicators may be due wholly or in part to variations in the degree of dispersion of the respective solutions, but Hantzsch [2] has been able to show that this explanation cannot be applied to methyl-orange and helianthine since these substances when perfectly pure do not form colloidal solutions with water.

[1] Zeitschr. Chem. Ind. Kolloide, **10**, 97.

[2] Ber., **46**, 1541 (1913).

For the more recent literature compare A. Thiele, "Die Anwendung neuerer Ergebnisse der Indikatorenforschung zu Quantitativen Studien," Sitzungsber. der Gesellschaft zur Beförd. der ges. Naturwissen zu Marburg, 1912; also N. Bjerrum, "Die Theorie der alkalimetrischen und acidimetrischen Titrierungen," Stuttgart, Encke, 1914.

CHAPTER XVIII

THE RELATIONSHIP BETWEEN FLUORESCENCE AND CHEMICAL CONSTITUTION [1]

Fluorescent substances are those which are luminous under the direct action of light; and such luminescence depends upon the fact that certain of the rays of light which strike the substance are transformed by it into others of different wave length. The manifestation of this phenomenon does not depend upon the state of aggregation but is common to solid, liquid, and gaseous substances. Fluorspar and uranium afford examples of the first class; paraffin oil and solutions of eosin, etc., examples of the second; and the vapors of sodium, iodine, etc., the third. If the effect is prolonged for a relatively long period after the source of light is withdrawn the phenomenon is known as phosphorescence. The two phenomena are, however, thought to be very closely related.

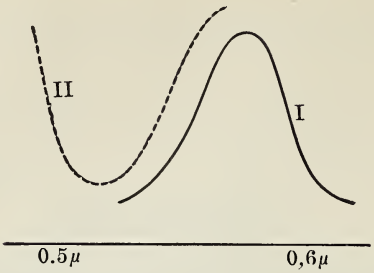
An important physical law governs all such phenomena—namely, that the light which radiates from a fluorescent body is not created by it, but represents absorbed rays which have been transformed. Stark [2] has recently discovered, as a result of his investigations in regard to line and band spectra, that fluorescence depends upon banded absorption, or, in other words substances which show this characteristic type of absorption also show the property of fluorescence.[3] Moreover, if a fluorescing ray is subjected to spectral analysis it is found to consist of one or more bands which usually possess a maximum intensity at certain wave lengths and this maximum corresponds to the maximum intensity of absorption for any given substance. This fact is shown by means of the following diagram [4] in which the ordinates represent the intensities of emitted and absorbed light:

[1] Compare Kauffmann, "Die Beziehungen zwischen Fluoreszenz u. chemischer Konstitution," Stuttgart, 1906.

[2] Physikal. Zeitschr., **8**, 81; **9**, 481, 661 (1908).

[3] Ley and Fischer, Ber., **46**, 327 (1913).

[4] Ley, "Farbe u. Konst.," p. 132.



Innumerable experiments seem to indicate that fluorescence is due to rays of higher refraction, as for example blue, violet, and ultraviolet. The less refractive rays such as yellow and red seem to be unable to produce the phenomenon. This so-called Stokes rule is not, however, without exceptions, and it has been observed that colored substances are quite frequently excited to fluorescence by waves of shorter length than the fluorescing waves which they emit.

Fluorescence may be most conveniently studied in the case of substances in solution since comparable conditions can most easily be maintained under these circumstances. Such investigations show that fluorescence depends to a marked degree upon the concentration of the dissolved substance and that it is usually strongest and clearest at great dilution. Increase in concentration is accompanied not only by a decrease in fluorescence but also frequently by a change in color—due possibly to the fact that the solution itself reabsorbs a part of the emitted light. Temperature represents still another factor governing fluorescence.

The mechanism of fluorescence has been made the subject of a very thorough investigation by E. Wiedemann,[1] whose views are very fully discussed in " Zur Mechanik des Leuchtens." Reasoning on the basis of the kinetic theory of gases he reaches the conclusion that fluorescence is due to the movements of certain atoms or groups of atoms in the molecule, which because of their particular functions can be called *fluorogens.*

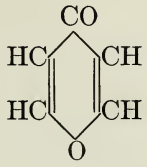
With the exception of the occasional utterances of a few investigators,[2] the first systematic study of the relation of fluorescence to chemical constitution was undertaken by Richard Meyer.[3] He was able to show that certain groups which he called *fluorophores* and which

[1] Annalen Physik., **37**, 188 (1889); **56**, 201 (1895); also E. Wiedemann, "Festschrift für Se. Kgl. Hoheit des Prinzregenten Luitpold von Bayern, dargebracht von der Universität Erlangen." Philosophische Fakultät, 2. Section, S. 35 (1911).

[2] Liebermann, Ber., **13**, 913 (1880).

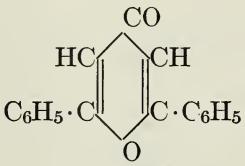
[3] Zeitschr. physikal. Chemie, **24**, 468 (1897).

are present in the molecules of such substances as the fluoresceins, xanthens, acridines, phenazines, phenoxazines, etc., are responsible for fluorescence in much the same way that chromophore groups are responsible for color. An enumeration of fluorophores includes the pyrone ring,



Pyrone

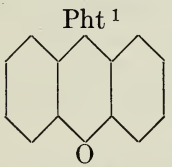
the azine-, oxazine-, thiazol-, rings, etc. Fluorescence is not, however, produced by the mere presence of such a group. It may be said in general that such phenomena are observed only in cases where a fluorophore occupies a position in the molecule between densely grouped atomic complexes such as C_6H_5, etc. Thus, for example, pyrone does not itself exhibit the property of fluorescence while α-α'-diphenylpyrone



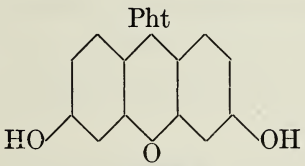
α-α'-Diphenylpyrone

belongs to the class of fluorescing substances.

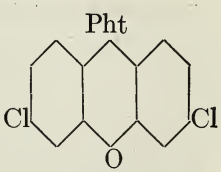
The effect of substitutions in the benzene ring is either to weaken or to destroy completely fluorescence, depending upon the nature of the substituting atom or group, as is shown in the case of



Fluorane,
strongly fluorescent

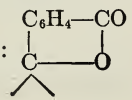


Fluoresceine,
weakly fluorescent

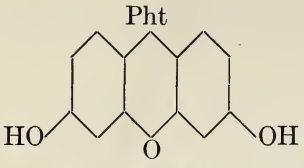


Dichlorfluorane,
only slightly fluorescent

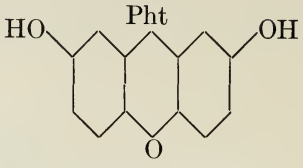
but depending also upon the position of such groups. Position is, in fact, a most important item, since only in the case of substitutions in certain definite positions does the fluorescence of the original substance

[1] Pht = Phthalyl—: 

persist. Thus, for example, only the first of the following two isomeric dehydroxyfluoranes shows the property of fluorescence:

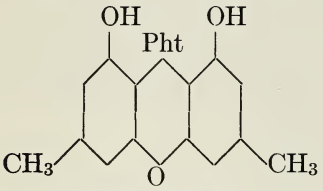


Fluoresceine

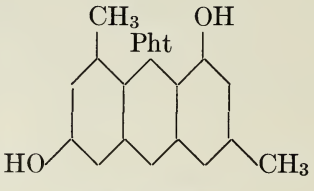


Hydroquinonphthaleine

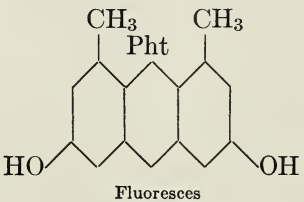
Substitution in other than specific and perfectly definite positions serves either to weaken greatly or else to destroy completely this property and in every case certain positions represent the maximum of fluorescence for any given derivative. This is further illustrated by the following set of three isomers:



Does not fluoresce



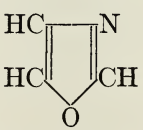
Does not fluoresce



Fluoresces

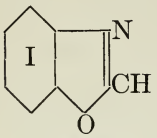
In the case of dissolved substances the nature of the solvent represents another important factor in fluorescence. Thus one and the same substance may fluoresce in certain solvents and not in others. Ionization may also play an important rôle in certain instances, but in others it is definitely excluded.

Interesting experimental evidence in support of Meyer's theory has been presented by F. Henrich,[1] who has demonstrated that the oxazol-ring



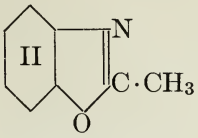
[1] Monatsh. Chemie, **19**, 492 (1898).

may function as a fluorophore in cases where the conditions of the theory are fulfilled. Thus in the case of benzoxazole and its derivatives:



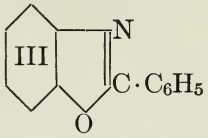
Benzoxazole

I



μ-Methylbenzoxazole

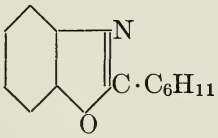
II



μ-Phenylbenzoxazole

III

it has been observed that the first exhibits the property of fluorescence and that the third, in which the fluorophore occupies a position between two phenyl groups, fluoresces strongly. The second, on the other hand, shows no trace of fluorescence. To what extent the difference between II and III depends upon the unsaturated character of the substituting group is shown by the fact that μ-hexahydrophenylbenzoxazole



resembles the corresponding methyl derivative in showing no trace of fluorescence.[1]

Later developments in the theory of fluorescence have taken place along the lines suggested by H. Kauffmann [2] as a result of his investigations in the field of luminescence. His conceptions of the relation between fluorescence and chemical constitution are based upon certain fundamental considerations and presuppose the presence of two special groups in the molecules of all fluorescing substances—namely a so-called *luminophore* and *fluorophore.*

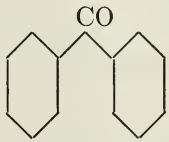
According to Kauffmann the luminophore must be regarded as the actual seat of fluorescence in that the fluorescing rays are supposed to originate there. The presence of such a group predisposes the molecule in which it is found to fluorescence, but it need not cause the manifestation of this phenomenon. For example, the benzene ring is a luminophore, but fluorescence in the case of aromatic compounds usually occurs only after the addition of a fluorophore to the molecule and then only under certain conditions. Thus aniline contains a luminophore but does not fluoresce, while anthranilic acid, on the other hand, fluoresces as the result of the introduction into the aniline molecular of a fluorophore carboxyl group in the *ortho* position.

[1] Ber., **37**, 3108 (1904).

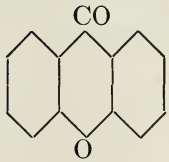
[2] Ber., **33**, 1731 (1900); **37**, 2941 (1904); **38**, 789 (1905); Annalen der Chemie, **344**, 30 (1906); Ahrens Sammlung, **11**, Vols. 1 and 2 (1906).

So long as the phenomenon was studied only in connection with substances possessing spectra in the visible region progress was slow but the discovery of fluorescence in the region of the ultra-violet, which could be accurately measured, gave fresh impetus to the development of the theory.[1] This discovery was due to the investigations of J. Stark,[2] who observed that benzene possessed a fluorescent absorption spectrum consisting of four bands in the region of the ultra-violet. He concluded that, since the majority of fluorescing substances are benzene derivatives, the ring itself must be regarded as the actual carrier of fluorescence in such compounds, or, in other words, that it is a *lumino-phore* in the sense in which this term is used by Kauffmann. The effect of substitution can be followed quantitatively in all such cases and it has been found in general to result in a definite shifting of the fluorescent bands away from the extreme ultra-violet in the direction of the red. Condensation of two or more benzene nuclei produces a similar result so that in passing from benzene → naphthalene → anthracene, for example, it has been found that fluorescence shifts progressively from ultra-violet in the direction of the longer wave lengths.[3]

In studying the effect of different substituting atoms or groups it has been found that the amido group exercises the strongest influence and following it the dimethylamido and hydroxyl groups. Auxochrome groups in general, as Kauffmann[4] maintains, represent an important factor in determining fluorescence. Ring formation represents another such factor, as is shown by the fact that while the fluorescent spectrum of benzophenone



is in the ultra-violet, the spectra of xanthine,



and its derivatives are either wholly or in part in the visible[5] region.

[1] Physikal. Zeitschr., **8**, 81 (1908).
[2] Physikal. Zeitschr., **9**, 481, 661 (1908).
[3] Physikal. Zeitschr., **8**, 250 (1908).
[4] "Die Valenzlehre," p. 494.
[5] Physikal. Zeitschr., **8**, 252 (1908).

The mechanism of the changes which are induced by substitution, and which in general tend to shift fluorescence from ultra-violet toward the visible may be accounted for in terms of Wiedermann's theory. Thus it may be assumed that, while in general the seat of fluorescence is the benzene ring as Stark and R. Meyer suppose, the particular manifestation observed in any given case is determined by the specific rate of vibration of the luminophore. If this vibration is slowed down as a result of substitution, the change will be perceptible in fluorescence of longer wave lengths. There is no reason, moreover, why this conception should not be extended to include the possibility of fluorescence in the infra-red as well as in the visible and ultra-violet.

The influence of substitution, salt formation, etc., upon fluorescence has recently been made the subject of special investigations by Ley [1] and also by H. Kauffmann.[2] According to Ley and his co-workers, Graefe and Englehardt, the fluorescent spectra of organic compounds absorbing in ultra-violet is very sensitive to slight changes in the constitution of the molecule. Exact measurements in ultra-violet show that the fluorescent spectrum of benzene changes in character as the result of any and every replacement of its hydrogen by substituting atoms or groups, i.e., the four separate absorption bands merge together into a single broad band and simultaneously absorption shifts in the direction of the red. In general substituents which tend to shift absorption in the direction of the longer wave lengths are called *bathoflore* groups while substituents having the opposite effect are called *hypsoflores*. Since intensity of absorption, is also affected, substituents may also be classified as *auxoflores* and *diminoflores*.

Material differences in the action of different groups may be readily accounted for on the basis of differences in their chemical character. Alkyl groups, for example, increase the intensity of fluorescent bands while halogens, on the other hand, weaken the intensity in direct proportion to their atomic weights although they have a negligible effect upon the position of the bands. This stands in marked contrast to the action of unsaturated groups such as OH, NH_2, CN, CH=CH, etc., where the effect is both auxofloric and bathofloric, as also of the COOH group where the effect is diminofloric and bathofloric. The presence of several substituents in the same molecule frequently has an additive effect although, of course, anomalies may result from the interaction of these groups upon each other.

An interesting case of anomaly has been observed in connection with

[1] Zeitschr. physikal. Chemie, **74**, 1 (1910); Ber., **41**, 2988 (1908); Zeitschr. wiss. Phot., **8**, 294; and "Farbe und Konstitution," p. 134.

[2] "Die Auzochrome," 1907, and also "Die Valenzlehre," p. 494.

certain nitrocompounds. Thus while it has been pointed out by R. Meyer [1] and H. Kauffmann [2] that nitro groups possess the power of destroying completely the fluorescence of a substance, certain notable exceptions to this general rule have been discovered. For example, while nitrobenzene and the nitrotoluene show no trace of ultra-violet fluorescence, and while the same is true of many radicals, such as picryl, $C_6H_2(NO_2)_3$, which contain nitro groups, nevertheless, picryl guanidine [3] and similar substances such as *m*-nitrodimethyl aniline,[4] etc., show strong fluorescence even in the visible spectrum. This striking difference between these two classes of nitro-compounds may be explained on the basis of anomaly by supposing that the specific action of nitro groups upon fluorescence is nullified by the interaction of nitro and amino groups accompanied by a saturation of the residual valencies within the molecule. As a result of this discovery it may be hoped that the affinity values of unsaturated groups will in the future be advantageously studied by means of a systematic investigation of fluorescent spectra.[5]

Naphthalene has, as Ley and Graefe [6] have discovered, a narrow band, almost line-like fluorescent spectrum, which changes to a single broad band and is at the same time shifted in the direction of the red as a result of the substitution of auxochromes such as NH_2 and OH,—thus showing a strong resemblance to benzene in its behavior. Saturated substituents such as alkyl groups and halides produce a single narrow banded spectrum with only slight displacement in the direction of the red. In general derivatives having substitutents in the β-positions fluoresce much more strongly than the corresponding α-substitution products.

Many of the fluorescing aromatic compounds form salts as, for example, $XNH_2 \rightarrow XNH_2HCl$, $XCOOH \rightarrow XCOONa$, $XOH \rightarrow XONa$, etc., where X represents C_6H_5, $C_{10}H_7$, etc.; and it has been observed in such cases that salt formation frequently has a marked and characteristic effect upon fluorescence. Such changes in fluorescence usually run parallel to corresponding changes in absorption but possess an advantage in that they are apt to show the character of the resulting intramolecular rearrangements in a much more striking manner. For example, neutralization with hydrochloric acid produces a strong

[1] Zeitschr.. physikal. Chemie, **24**, 481 (1897).

[2] "Beziehungen zwischen Fluoreszenz und chemischer Konstitution," 1906, p. 80.

[3] Ber. **41**, 1637 (1908).

[4] Ber., **40**, 2341 (1907); **41**, 4396 (1908).

[5] "Farbe und Konstitution," pp. 136–157.

[6] Ibid.

diminution in fluorescence in the case of aniline while the presence of an excess of acid completely destroys this property. The same is true of organic acids so that benzoic, α-and β-naphthoic acids, etc., gradually lose their fluorescence on the addition of alkali. In every instance diminution in fluorescence is accompanied by a shifting of the absorption in the direction of the ultra-violet, thus indicating in general that salt formation involves fundamental alterations in structure.

The intense fluorescence of phenol and naphthol, while considerably lessened by neutralization, never completely disappears even in the presence of an excess of alkali, apparently showing that salt formation in these cases is different in type from that involved in the instances previously cited.

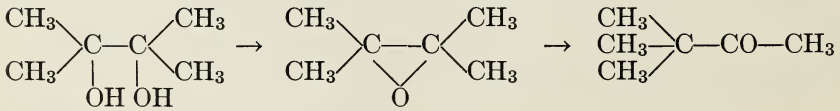
CHAPTER XIX

MOLECULAR REARRANGEMENTS

Molecular rearrangements have been considered previously in connection with a study of the phenomena of tautomerism and desmotropism. Such changes, however, did not involve the skeleton of carbon and nitrogen atoms constituting the molecule, and dealt only with the nature of the union between the atoms, which shifted backward and forward between certain positions in the molecule. Rearrangements must be considered now where variations in the molecular structure are accompanied by dissociation of the molecule and wandering not only of an individual atom but also of whole groups of atoms or radicals. Transformations of this type are very common in organic chemistry. In fact they were observed in the very beginning of the scientific development of this subject for the classic synthesis of urea, which was discovered by Wöhler, depends upon a molecular rearrangement of ammonnium cyanate

$$CONNH_4 \rightarrow C(=O)(NH_2)_2$$

Molecular changes may be similar to the transformation of ammonium cyanate into urea, or ammonium thiocyanate into thiourea—i.e., where one substance merely isomerizes or passes over into another without loss of atoms—or they may be accompanied by the elimination of such groups of atoms as constitute the halogen acids, H_2O, N_2, etc. In the latter instances the existence of intermediate substances, isomeric with the original substance or with the product which is formed, may be assumed. Such a rearrangement is illustrated by the transformation of pinacone into pinacoline:



Molecular rearrangements, even at the present stage of development of chemistry, offer difficulties of interpretation from the point of view

of the theory of organic structure; for frequently changes must be represented as taking place abruptly and involving a dissociation of the molecule, and not in gradual stages where the intermediate steps may be followed easily. It is, therefore, difficult and even impossible in many cases, to express the nature of the molecular transformation in terms of our accepted structural theory.

It is to be noted that the phenomenon of rearrangement is always associated with quite definite groups of atoms which may represent the whole or a part of the organic molecule. In those cases where two isomeric forms are capable of existing simultaneously and independently under given conditions of temperature and pressure, the cause of the change from a labile to a stable modification may be accounted for by supposing that one isomer possesses a higher energy content than the other, and so, under favoring circumstances, physical or chemical in nature, that transformation generally takes place which involves a loss of energy. Such changes may be brought about with very great ease, or may be induced only by the action of energetic chemical reagents catalysts. At present there is no theory which covers every form of isomeric change.

The most important classes of molecular rearrangements may now be considered. It is extremely difficult to devise a system of classification for the various types of rearrangement that have been discovered. There are, however, certain generalities of fundamental importance, and if these are taken into consideration a partial classification can be made which enables one to present this work in a logical manner.

Rearrangements of the Cyanic and Thiocyanic Acid Series:

These transformations are brought about generally and preferably by the action of heat.

$$NH_4NCO \rightarrow CO(NH_2)_2$$

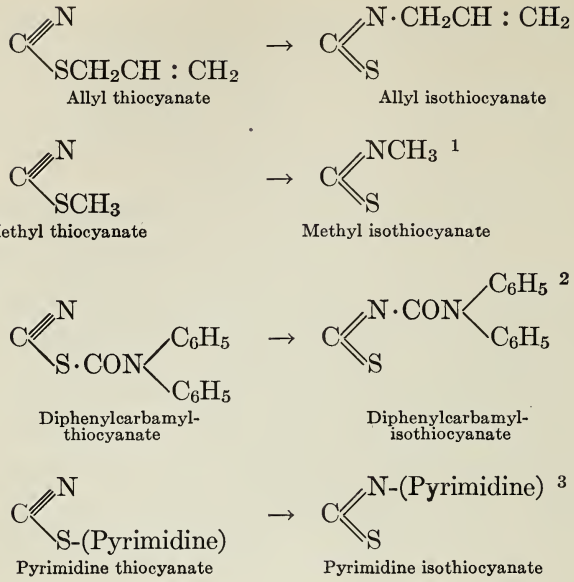
Ammonium cyanate — Urea

$$HNCO \cdot NH_2 \cdot NH_2 \rightarrow CO(NH_2)(NH \cdot NH_2)$$

Hydrazine cyanate — Semicarbazide

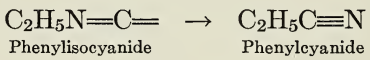
$$NH_4SCN \rightarrow CS(NH_2)_2$$

Ammonium thiocyanate — Thiourea

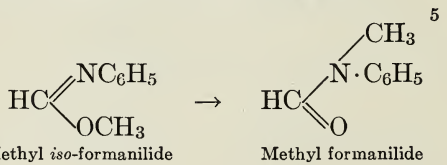


Cyanic esters corresponding to the thiocyanates or rhodanides have not been isolated. Many cases are known where the isothiocyanate form is the only modification of the rhodanide that can be isolated. Also thiocyanates are known which cannot be rearranged into their corresponding isothiocyanates. These rearrangements are not reversible, so far as can be concluded from experimental evidence presented up to the present time.

Isocyanides undergo isomerization to give the cyanides

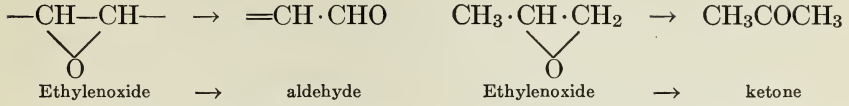


or acid nitriles. To these may be added the rearrangements of imido esters, which will be referred to latter in this text.

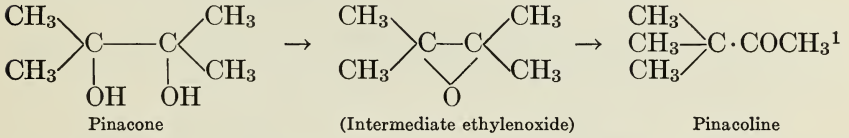


[1] Hoffmann, Ber., **13**, 1350 (1880); see also Jour. prakt. Chemie, **37**, 506 (1880).
[2] Johnson and Levy, Am. Chem. Jour., **38**, 456 (1907).
[3] Johnson and Storey, Am. Chem. Jour., **40**, 131 (1908).
[4] Nef, Annalen der Chemie, **280**, 296 (1894).
[5] Wheeler and Johnson, Am. Chem. Jour., **21**, 185 (1899).

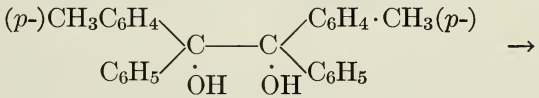
Rearrangements involving the Transference of Radicals from Carbon to Carbon:



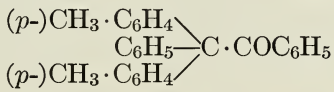
Changes of the above type are brought about by heat and by the action of catalysts. The so-called pinacoline rearrangement also belongs to this class and may be represented as follows:



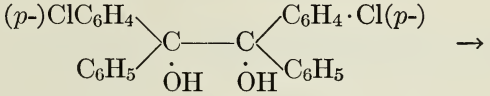
Conversions of this kind are very common, and certain definite rules have been formulated in regard to the wandering of different groups of atoms. Some of these may be mentioned briefly. The pinacone,



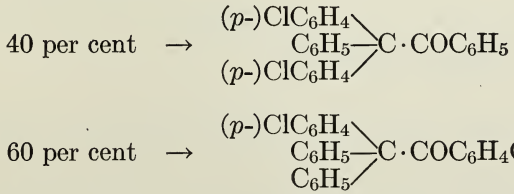
rearranges to give exclusively:



From which it is obvious that the tolyl group shifts its position more readily than the phenyl. With halogen substitution products the course of the raction is different and a mixture of ketones is obtained. For example:



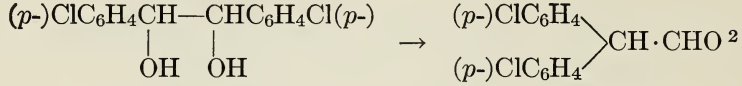
gives



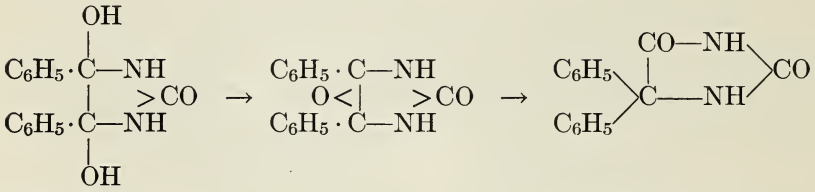
[1] Jour. russ. physikal. Chem. Ges., **34**, 537; Biltz and Seydel, Ber., **46**, 138 (1913); Meerwein, Annalen der Chemie, **396**, 206 (1913); **405**, 129 (1914); **417**, 255 (1918); **419**, 121 (1919).

From this result the conclusion may be drawn that the phenyl group shifts its position more readily than the *p*-chlorphenyl.[1]

If all four hydrogen atoms of glycol have not been substituted by carbon residues, rearrangement results in the formation of aldehydes. The following example illustrates how the wandering of the atoms takes place in this type of compounds:

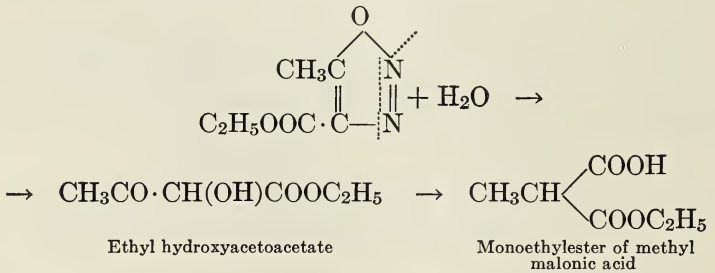


To this series of rearrangements belongs also the unique cyclic pinacone rearrangement described by Biltz:[3]



Diphenylglyoxalonglykol — Diphenylhydantoin

An interesting rearrangement closely related to this series is that described by Wolff[4] in which a hydroxyl group and a methyl radical are assumed to exchange positions in the molecule when the anhydride of ethyl diazoacetoacetate is subject to hydrolysis:



Ethyl hydroxyacetoacetate — Monoethylester of methyl malonic acid

A similar transformation is brought about by the action of water on the anhydride of diazobenzoylacetone:

[1] Acree, Am. Chem. Jour., **33**, 189 (1905); Hoogewerff and vanDorp, Rec. trav. chim. des Pays-Bas. **9**, 225 (1890); Montagne, ibid., **24**, 105 (1906); **26**, 256 (1907).

[2] Rec. trav. chim. des Pays-Bas., **21**, 30 (1902).

[3] Ber. **41**, 1379 (1908). See also Montagne, Rec. trav. chim. des Pays-Bas., **21**, 6 (1902); Ber., **51**, 1479 (1918).

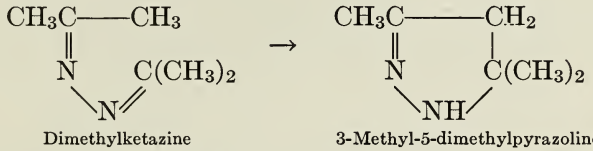
[4] Annalen der Chemie, **325**, 144 (1902).

The rearrangement of halogen from carbon to carbon in the aliphatic series is illustrated in the following case observed by Hantzsch and Conrad.[1] This change is brought about under the influence of hydrobromic acid.

$$CH_3CO\cdot CHBrCOOC_2H_5 \rightarrow BrCH_2COCH_2COOC_2H_5$$

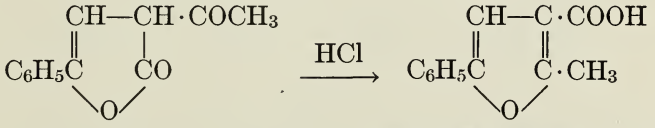
Ethyl α-bromacetoacetate. Ethyl γ-bromacetoacetate.

A rearrangement involving the formation of a ring by linking together two carbon atoms is shown below:[2]



Dimethylketazine 3-Methyl-5-dimethylpyrazoline

Borsche and Fels record the following unique rearrangement in the furane series.[3] Here we are dealing with the formation of an intermediate acyclic compound, which condenses again with formation of a new cycle:

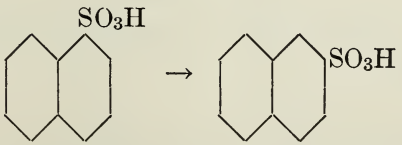


Methyl-phenyl-furanecarboxylic acid

Rearrangements involving the migration of alkyl radicals or halogen from carbon to carbon, and brought about by the agency of aluminium chloride, belong to this class.

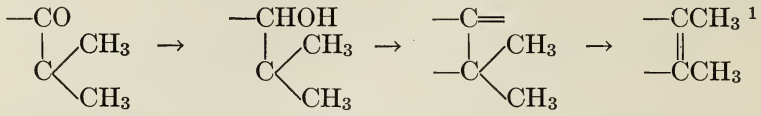
$$CH_3CH_2CH_2Br \rightarrow CH_3CHBr\cdot CH_3$$ [4]

Sulphonic acid groups also change their positions in the benzene ring under certain conditions.[5] Such transformations have been very commonly observed in the aromatic series.

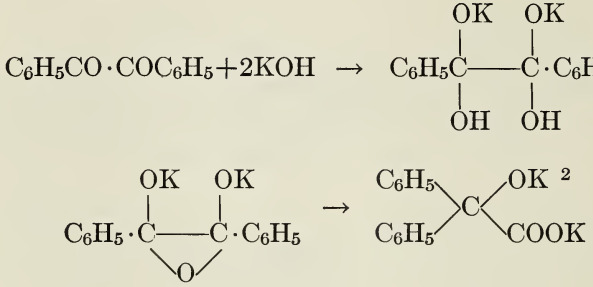


[1] Ber., **27**, 355, 3168 (1894); Ber., **29**, 1042 (1896); Ber., **36**, 2251 (1903).
[2] Curtius and Zinkeisen, Jour. prakt. Chemie, **58**, 310 (1898).
[3] Ber., **39**, 1809 (1906).
[4] Gustavson, Ber., **16**, R. 957 (1883); **20**, 707 (1887).
[5] Schramm, Ber., **21**, 782 (1888).

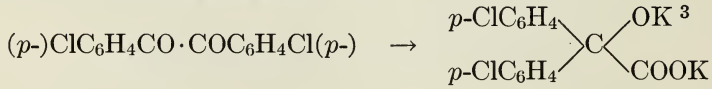
Several cases have been recorded in the chemical literature where a methyl group migrates from carbon to carbon during the process of reduction:



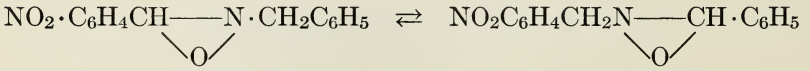
Benzilic acid rearrangements, which take place when *ortho* diketones are fused with potassium hydroxide, may be regarded as belonging to this class, if the course of the transformation is formulated as follows:



In this type of change, as in the pinacone rearrangements, a chlorine atom maintains its *p*-position in the benzene nucleus in relation to the corresponding carbon atom during the shifting of the groups. This is shown by the following example:



Nitrogen alkyl derivatives of isoaldoximes undergo rearrangements which are reversible:



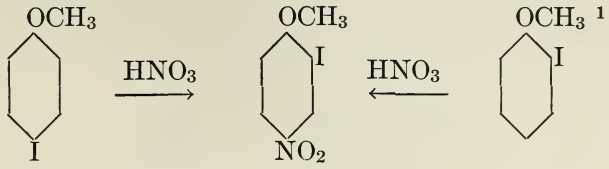
[1] Brunner, Monatsh. Chemie, **17**, 276 (1896); **21**, 156 (1900); Baeyer, Ber., **32**, 2429 (1899); Wolff, Annalen der Chemie, **322**, 351 (1902); Knorr, Ber., **36**, 1272 (1903).

[2] Tiffeneau, Revue gén. Sci. pur. et appli., 1907, p. 585.

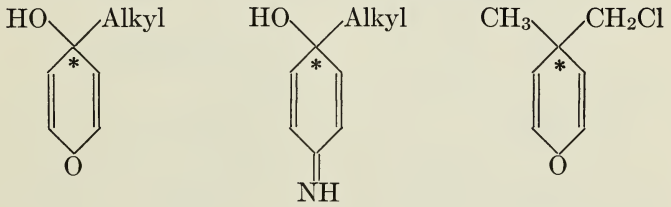
[3] Rec. trav. chim. des pays-Bas, **21**, 19 (1902); see also Ber., **38**, 3738 (1905).

[4] Neubauer, Annalen der Chemie, **298**, 187 (1897).

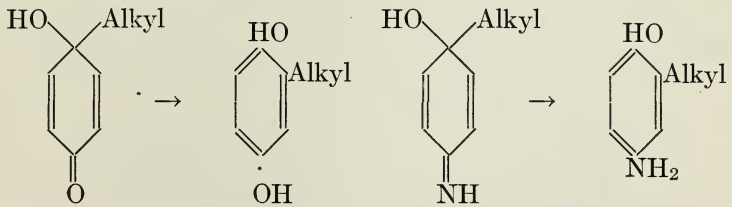
The rearrangement of iodine in benzene compounds is often met with as is illustrated in the behavior of *p*-iodanisol towards nitric acid:



Quinole Rearrangements: An exceptionally reactive group of substances was discovered as the result of the investigations of Zincke, E. Bamberger and Auwers.[2] They received the name of "quinoles" because of their semi-quinoidal nature. They are obtained from *para* substituted phenylhydroxylamines and are referred to in the class of rearrangements involving migration of radicals from nitrogen to carbon. The following types may be taken as examples:



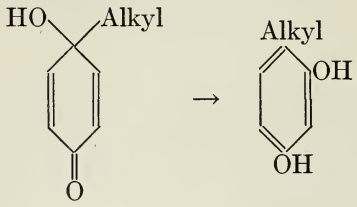
In these compounds either of the two groups bound to the carbon atom indicated by *, may shift its position. To illustrate, the alkyl group in I or II may wander into the nucleus and there assume another position. This happens when the substance is treated with aqueous sulphuric acid or sodium hydroxide:



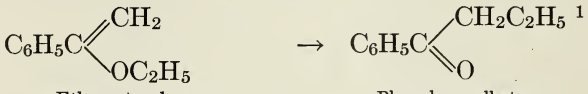
[1] Reverdin, Ber., **29**, 2595 (1896); **30**, 2999 (1897).

[2] Zincke, Ber., **28**, 3121 (1895); **34**, 253 (1901); Annalen der Chemie, **320**, 145 (1901); **322**, 174 (1902); **325**, 19 (1902); **329**, 1 (1903); **330**, 61 (1904); Bamberger, Ber., **33**, 3600 (1900); **35**, 1424, 3886 (1902); **36**, 1625, 2028 (1903) Auwers, Ber., **35**, 443, 455, 465, 4207 (1902); **36**, 1861, 3902 (1903).

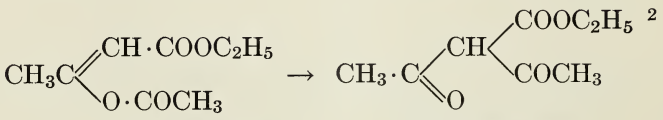
If, on the other hand, the compound I, for example, is treated with alcoholic sulphuric acid, the product of rearrangement consists of the alkyl derivative of a substance which now contains an hydroxyl group in the *ortho* position of the benzene nucleus. In other words, either the hydroxyl or alkyl group can be rearranged at will.



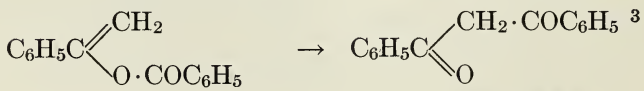
Rearrangements Involving the Transference of Radicals from Oxygen to Carbon: Several rearrangements of this type have been observed in the aliphatic series.



α-Ethoxystyrol — Phenylpropylketone [1]

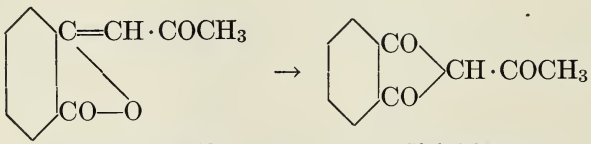


Ethyl diacetoacetate [2]



Dibenzoylmethane [3]

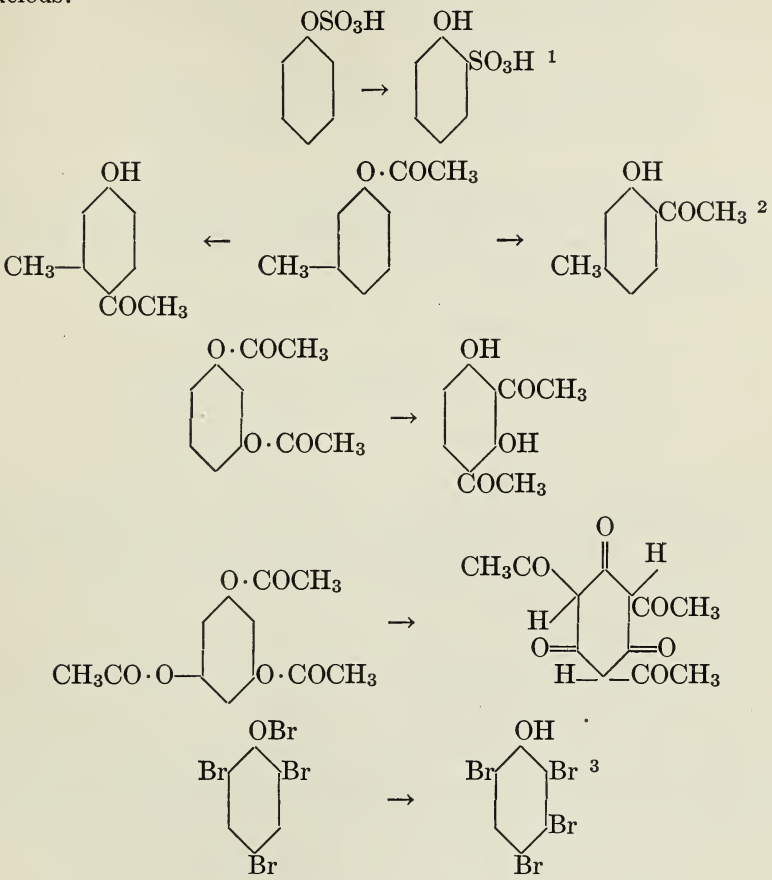
A rearrangement of similar type in the cyclic series is that described by Bülow: [4]



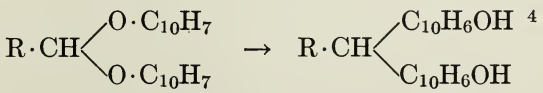
Acetonyl-phthalide — Phthalylacetone

[1] Ber., **29**, 2931 (1896).
[2] Claisen and Haase, Ber., **33**, 1242 (1900); Ber., **36**, 3674, 3778 (1903).
[3] Claisen, Ber., **36**, 3674 (1903).
[4] Ber., **37**, 4380 (1904).

To this class belong a number of the rearrangements which phenol ethers and esters undergo when acted upon by heat or by catalytic agents, and which give rise to phenols with substitution in the benzene nucleus:



Rearrangements of phenol ethers into alkylated phenols belong to this class, and are brought about by application of heat or by the action of acids:

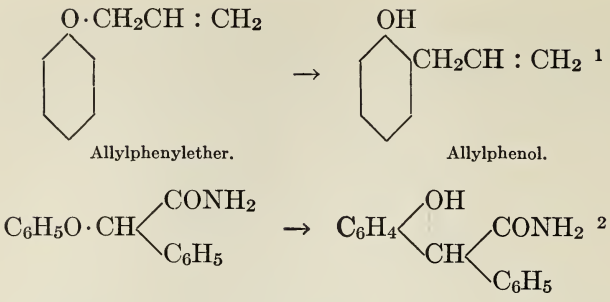


[1] Baumann, Ber., **9**, 55, 1715 (1876).

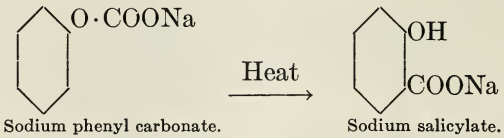
[2] Eijkman, Chem. Centralbl., 1904, I, 1597; 1905, I, 814; also Heller, Ber., **42**, 2736 (1909); **45**, 418 (1912).

[3] R. Benedikt, Annalen der Chemie, 199, 127 (1879).

[4] Claisen, Annalen der Chemie, **237**, 261 (1887).



Kolbe's synthesis of salicylic acid from phenol and carbon dioxide is based on a metameric change involving the transfer of a carboxyl group from oxygen to carbon:



Rearrangements Involving the Transference of Radicals from Nitrogen to Carbon: Transformations of this type are brought by heat, by catalytic agents, and by the action of mineral acids. They are observed very frequently in the case of aromatic compounds and heterocyclic combinations.

To this class belong the rearrangements of alkyl anilines, discovered by A. W. Hofmann and Martius.[3] It was observed that the halogen salts of secondary and tertiary aromatic amines, as well as quaternary ammonium salts, when heated at 200° to 350° in the presence of alcohol suffer an intramolecular change, whereby the substituting groups wander into the benzene nucleus, assuming *o*- and *p*-, but never *m*-, positions.

$$C_6H_5NHC_2H_5 \cdot HCl \rightarrow C_2H_5C_6H_4NH_2 \cdot HCl$$

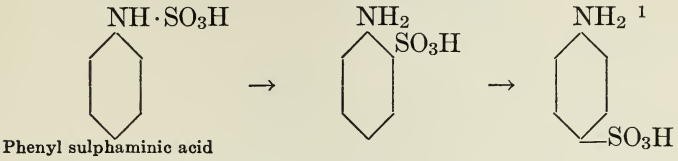
In this type of rearrangement there is very good reason for supposing that the original substance breaks down at the high temperature to form aniline and the alkyl halide, which then recombine to form an isomeric product with the substituting alkyl group in the benzene

[1] Claisen and Eisleb, Annalen der Chemie, **401**, 21 (1913); Ber. **45**, 3157.

[2] Bucherer and Grolée, Ber., **39**, 1012 (1906).

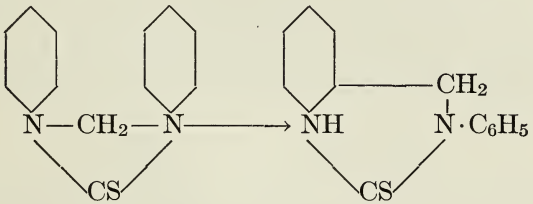
[3] Hofmann, Ber., **4**, 742 (1871); **5**, 704, 720 (1872); **7**, 526 (1874); **18**, 1821 (1885); Nölting and Baumann, Ber., **18**, 1149 (1885); Nölting and Forel, Ber., **18**, 2680 (1885); Limpach, Ber., **21**, 640, 643 (1888); Hodgkinson and Limpach, Jour. Chem. Soc., **61**, 420 (1892); Benz, Ber., **15**, 1646 (1882).

nucleus, but in the following instances genuine intramolecular rearrangements involving dissociation of the molecule seem fairly certain:

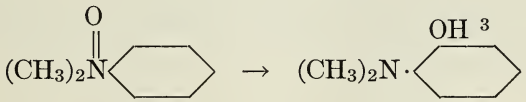


Phenyl sulphaminic acid

Another arrangement of this class is that described by Senier and Shepheard,[2] and also that of the



aromatic amine-oxides, which have been shown to undergo rearrangement to hydroxyanilines as is represented below:



Phenyl sulphaminic acid rearranges to give first the *o*-, and then *p*-sulphonic acid derivative of aniline. The former reaction takes place at low temperatures in the presence of dilute acids; and the latter on the addition of concentrated acids. If phenyl sulphaminic acid is treated directly with concentrated sulphuric acid, it passes into the *p*-sulphonic acid (sulphanilic acid) and no *o*-sulphonic acid is formed. The complete transformation involves, therefore, a migration of the sulphonic acid radical from nitrogen to carbon and finally a second change from carbon to carbon.

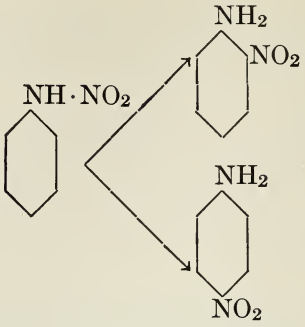
Aromatic nitroamines rearrange to form nitro-anilines.[4]

[1] Bamberger and Kunz, Ber., **30**, 654, 1261, 2277 (1897).

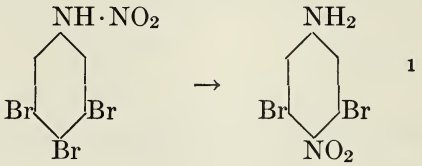
[2] Jour. Chem. Soc., **95**, 494 (1909).

[3] Bamberger and Tschirner, Ber., **32**, 1889 (1899).

[4] Bamberger, Storch and Landsteiner, Ber., **26**, 471, 485 (1893); **27**, 584 (1894); **28**, 401 (1895); **30**, 1252 (1897); Stoermer, Ber., **31**, 2528 (1898).

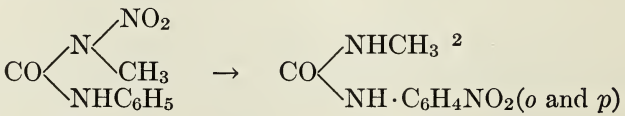


Here the nitro group wanders independently to two different positions in the benzene ring, since *o*-nitroaniline cannot be rearranged into the *p*-modification. In these rearrangements the nitro group in migrating will even force another group from its position in the benzene ring:



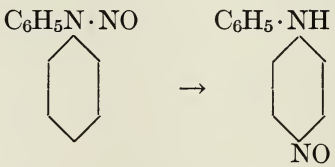
[1]

α-nitro-α-methyl-β-phenylurea rearranges by the action of cold concentrated sulphuric acid to give a mixture of α-methyl-β-*ortho*- and *para*-nitrophenylureas:



[2]

Aromatic nitrosamines rearrange to give *p*-nitroso derivatives of aniline,[3] (Otto Fischer-Hepp rearrangement):

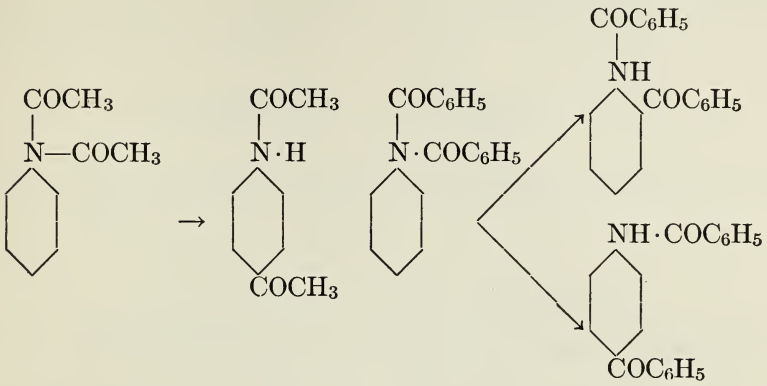


[1] Orton and Smith, Jour. Chem. Soc., **87**, 389 (1905).

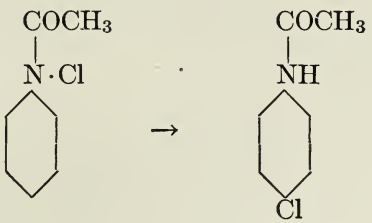
[2] Scholl and Nyberg, Ber., **39**, 2491 (1906).

[3] O. Fischer and Hepp, Ber., **19**, 2991 (1886); **20**, 1247 (1887); O. Fischer, Ber., **45**, 1098 (1912).

Brombenzene diazonium chlorides undergo molecular transformations with change of position of the halogen, and the diacylanilides, on heating, pass over into acylamidoketones.[1]



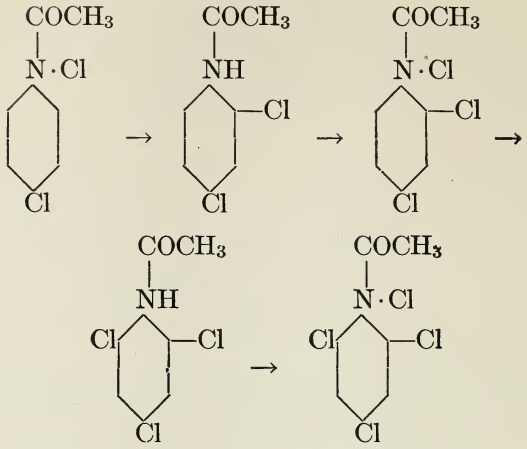
Although in the case of these anilides, only one substituting group enters the benzene ring, there are instances where two or more groups may enter the benzene nucleus as the result of rearrangements. Thus *N*-chlor-acetanilides rearrange to form *p*-and *o*-chloracetanilides:[2]



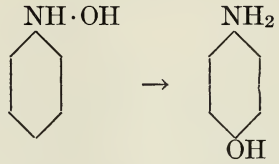
The *p*-chloracetanilide formed may now be changed into N-chlor-*p*-chloracetanilide, and this in turn may rearrange so that the chlorine atom shifts from nitrogen and replaces a second hydrogen atom in the ring. The process may be repeated until the hydrogen atoms occupying the *p*- and the two *o*-positions in the benzene ring, as well as the hydrogen in union with nitrogen, have been replaced by chlorine. Chlorine does not shift to the *m*-position.

[1] Chattaway, Jour. Chem. Soc., **85**, 388 (1904).

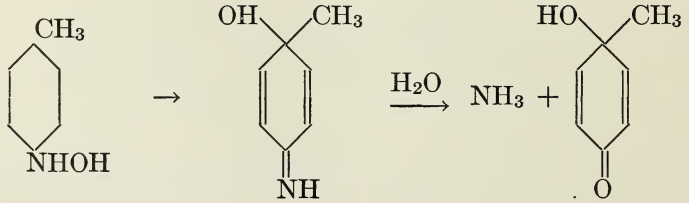
[2] Chattaway and Orton, Ber., **32**, 3573, 3635 (1899); Blanksma, Rec. trav. chim. des Pay-Bas, **21**, 329 (1902); Hantzsch and Smythe, Ber., **33**, 505 (1900).



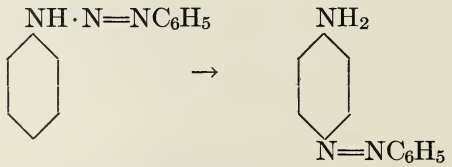
Phenylhydroxylamines rearrange to form *p*-amidophenols:[1]



When the hydrogen in the *para* position is substituted in these hydroxylamine combinations, rearrangement takes place with formation of quinoles, since the hydroxyl radical does not migrate to an *ortho* or *meta* position in such cases:



Diazoamido compounds rearrange to form amidoazo compounds:

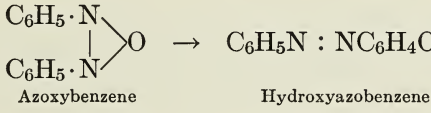


[1] Gattermann, Ber., **26**, 1845 (1893); Wohl, Ber., **27**, 1432 (1894); Lagutt, Ber., **31**, 1501 (1898).

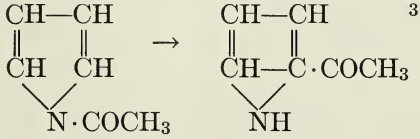
In the case of this reaction also, it has not yet been possible to establish the fact that a genuine intramolecular rearrangement takes place, and to exclude the possibility of a decomposition of the compound by heat, accompanied by secondary processes involving recombinations of the groups thus formed. The following rearrangements of diazo compounds are also known to take place: [1]

$$Br_3C_6H_2N : NCl \rightarrow Br_2ClC_6H_2N : N \cdot Br$$

When heated with sulphuric acid azoxybenzenes rearrange according to the following scheme:



Pyrrol rearrangements should be mentioned at this point.



$$C_4H_4NCH_3 \rightarrow CH_3 \cdot C_4H_3 \cdot NH \ [4]$$

As is well known A. Pictet was able to carry through successfully a synthesis of nicotine on the basis of such a pyrrol rearrangement.

In addition to these rearrangements which have been recorded the semidine and also the benzidine rearrangements should be mentioned. The benzidine change is one of great commercial importance. There are innumerable instances of changes of both types to be found in the chemical literature,[5] but one illustration in each case will suffice here, thus:

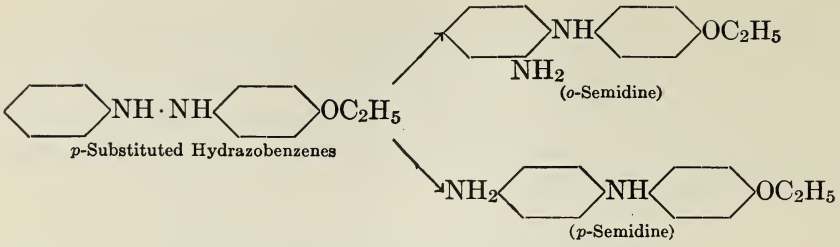
[1] Hantzsch, Schleissing and Jäger, Ber., **30**, 2337 (1897); Hantzsch and Smythe, Ber., **33**, 505 (1900).

[2] Wallach and Kiepenheuer, Ber., **14**, 2617 (1881).

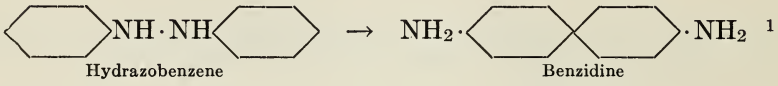
[3] Ciamician and Silber, Ber., **18**, 881, 1828 (1885); **19**, 1962 (1886); **20**, 698 (1887); **22**, 659, 2518 (1889).

[4] Pictet, Ber., **38**, 1951 (1905).

[5] Jacobson and Fischer, Ber., **25**, 992 (1892); **26**, 681, 688, 699, 703 (1893); **27**, 2700 (1894); Annalen der Chemie, 287, 97 (1895); Täuber, Ber., **25**, 1019 (1892); Witt and Schmidt, Ber., **25**, 1013 (1892); **27**, 2351, 2358 (1894).



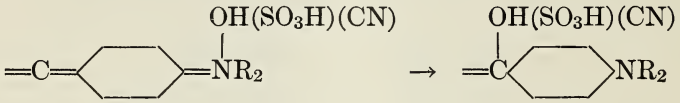
and



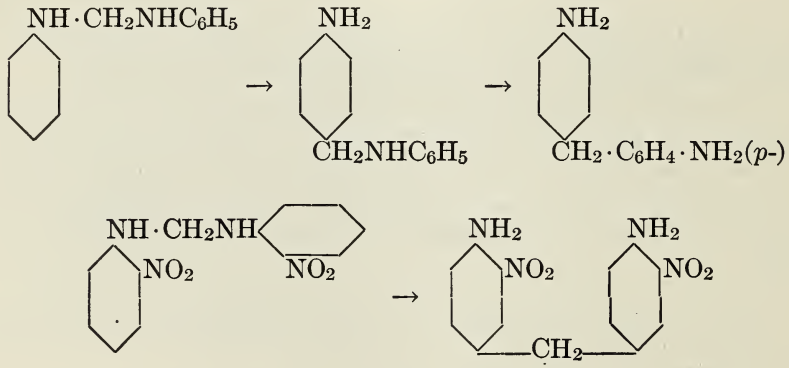
[1]

Stieglitz [2] interprets this change as taking place through dissociation into free radicals while Wieland [3] disagrees with this conclusion.

Aromatic ammonium hydroxides, sulphonic acids, and cyanides of quinoid structure rearrange to form tertiary amino combinations:



The rearrangement of methylene dianilines into derivatives of diphenylmethane is brought about by the action of acids: [4]



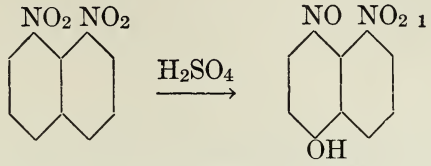
[1] Zinin, Jour. prakt. Chemie, **36**, 93 (1863).

[2] Ber., **46**, 911 (1913); Jour. Amer. Chem. Soc., **35**, 1143 (1913).

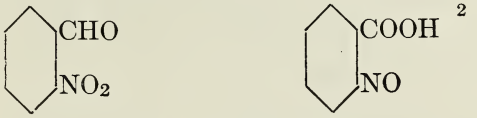
[3] Ber., **48**, 1100 (1915).

[4] Eberhardt and Welter, Ber., **27**, 1810 (1894); Meyer and Rohmer, **33**, 250 (1900); Von Braun and Krules, Ber., **45**, 2977 (1912).

Rearrangements involving intramolecular oxidation have also been observed in the aromatic series:



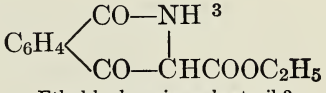
1, 8-Dinitronaphthalene — 1-Nitro-8-nitroso-5-hydroxynaphthalene [1]



[2]

Ethyl phthalimidoacetate also loses its identity when acted upon by sodium ethylate:

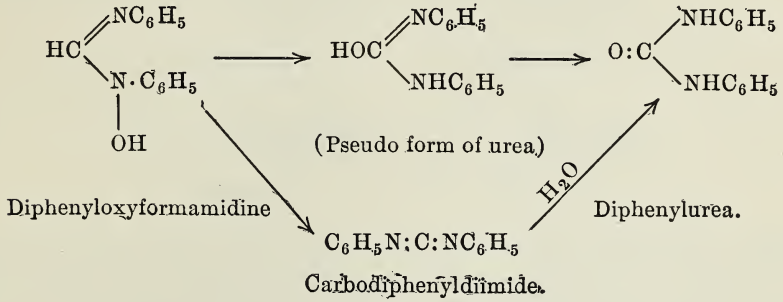
Ethyl phthalimidoacetate



[3]

Ethyl hydroxyisocarbostyril-3-carboxylate

Mention should also be made here of the rearrangement of hydroxyformamidine combinations into ureas.[4]



Diphenyloxyformamidine — Diphenylurea.

Carbodiphenyldiimide.

This rearrangement is brought about by the action of acetic anhydride. Whether it involves a molecular exchange of the hydrogen and hydroxyl groups, or a dehydration of the molecule with intermediate formation of carbodiphenyldiimide has not been established.

[1] Friedlander and Scherzer, Chem. Centralbl. (1900), **I**, 409.
[2] Weigert and Kummerer, Ber., **46**, 1207 (1913).
[3] Gabriel and Colman, Ber., **33**, 980 (1900); **35**, 1358 (1902).
[4] Bamberger, Tschirner and Destraz, Ber., **35**, 720, 1874 (1902).

Rearrangements involving the Transference of Radicals from Nitrogen to Nitrogen: To this series belong the interesting changes which were discovered and elucidated by M. Busch and his students, i.e., those involved in the reaction between mono alkylated hydrazines

$$R \cdot NH \cdot NH_2$$

and isocyanates, or isothiocyanates (R·NCO and R·NCS). Contrary to views previously held, these investigators have demonstrated experimentally that the primary products of these reactions are respectively semicarbazides and thiosemicarbazides, the formation of which may be expressed by the equation:

$$RNH \cdot NH_2 + (S)OCNR'' = \begin{matrix} RN \cdot NH_2 \\ | \\ CO(S)NHR'' \end{matrix}$$

If, now, R = alphyl (i.e., an aliphatic alkyl group), the resulting α-semicarbazides and α-thiosemicarbazides are stable bodies. If, however, R = aryl (i.e., an aromatic alkyl group), the primary product is unstable and the substituted carbamyl or thiocarbamyl radical will shift from the α-nitrogen to the β-position in the molecule.[1] This will happen in alcohol solution or upon fusion:

$$\begin{matrix} {}^{\alpha}RN \cdot {}^{\beta}NH_2 \\ | \\ CONHR' \end{matrix} \rightarrow \begin{matrix} {}^{\alpha}RNH \cdot {}^{\beta}NH \\ | \\ CONHR' \end{matrix}$$

and

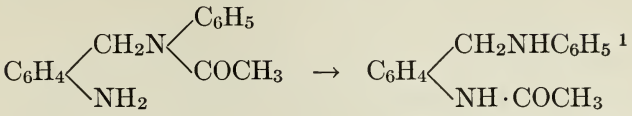
$$\begin{matrix} {}^{\alpha}RN \cdot {}^{\beta}NH_2 \\ | \\ CSNHR' \end{matrix} \rightarrow \begin{matrix} {}^{\alpha}RNH \cdot {}^{\beta}NH \\ | \\ CSNHR' \end{matrix}$$

Further, M. Busch and O. Limpach[2] have discovered a remarkable rearrangement which takes place when phenyl mustard oils react with esters of phenylcarbazinic acid and which involves a shifting of a carbethoxy group in an opposite direction ($\beta \rightarrow \alpha$) to that shown above:

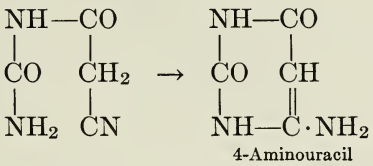
$$\underset{\text{Ethyl phenylcarbazinate}}{C_6H_5NH \cdot NHCOOC_2H_5} + SCNC_6H_5 \rightarrow \begin{matrix} & & COOC_2H_5 \\ & & | \\ C_6H_5N \cdot & NH \\ & | \\ & CSNHC_6H_5 \end{matrix}$$

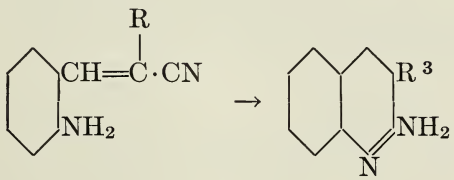
[1] Ber., **34**, 320 (1901); **36**, 1362 (1903); **37**, 2318 (1904); **42**, 4596, 4602 (1909).
[2] Ber., **44**, 1573 (1911).

Other rearrangements of this series are as follows:

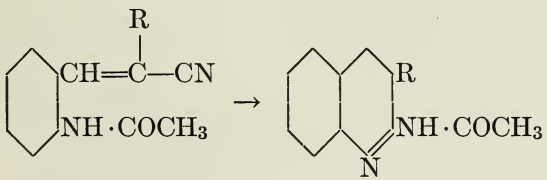


Nitriles of *o*-aminocinnamic acids rearrange to quinoline compounds. An analogous change is met with in the transformation of cyanacetylureas into pyrimidine combinations:[2]

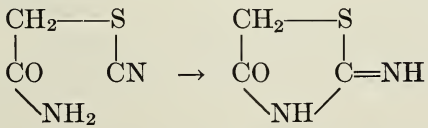




Acyl derivatives of these nitriles undergo similar transformations with migration of the acyl group to a different nitrogen atom.

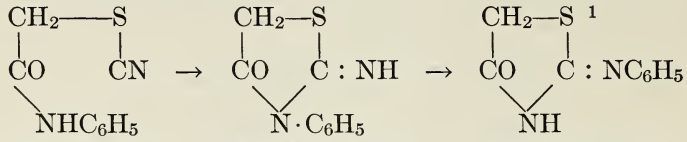


Thiocyanacetanilide rearrangements belong in this series. Thiocyanacetamide isomerizes to a cyclic combination.[4]



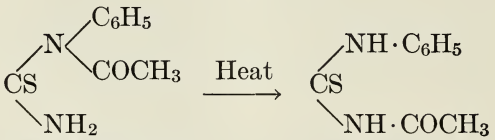
[1] Widman, Jour. prakt. Chemie, **47**, 354 (1893).
[2] W. Traube, Ber., **33**, 3035 (1900).
[3] Pschorr and Wolfes, Ber., **32**, 3399 (1899).
[4] Miolati, Gazz. chim. ital., **23**, 90 (1893); Chem. Centralbl. (1893), I, 640.

Substituted thiocyanacetamides or anilides undergo similar transformations giving unstable pseudothiohydantoins, which can rearrange further into stable modifications. These transformations can be brought about by heating with or without solvents, and in many cases the labile modifications of the hydantoin cannot be isolated. Isothiocyanacetamide and the corresponding anilides have not been prepared.



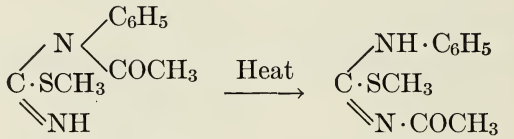
Thiocyanacetanilide — Unstable form of phenyl pseudothiohydantoin — Stable form of phenyl pseudothiohydantoin

In this series belong also the following important types of molecular rearrangements: *unsym*-acylthioureas are rearranged easily by heat into their stable *sym*-modifications: [2]

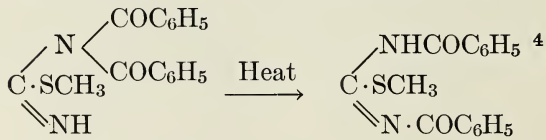


Unsym.-acetylphenyl-thiourea — *Sym*.-acetylphenyl-thiourea

and this is also true of the pseudothioureas: [3]



Unsym.-Acetylphenyl pseudomethylthiourea — *Sym*.-Acetylphenyl-pseudomethylthiourea



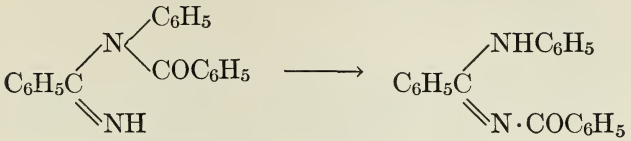
[1] Wheeler and Johnson, Am. Chem. Jour., **28**, 121 (1902), Johnson, Jour. Am. Chem. Soc., **25**, 482 (1903); Walther and Stenz, Jour. prakt. Chemie, **61**, 575 (1900).

[2] Wheeler, Am. Chem. Jour., **27**, 270 (1902); Hugershoff, Ber., **32**, 3649 (1899).

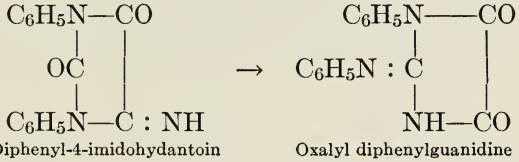
[3] Wheeler and Johnson, Am. Chem. Jour., **27**, 274 (1902).

[4] Johnson and Jamieson, Am. Chem. Jour., **35**, 297 (1906).

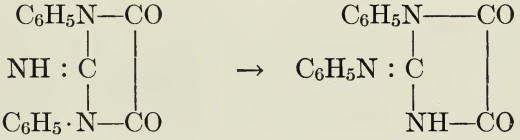
Unsym. acylamidines likewise rearrange to their *sym.* forms:[1]



Rearrangements involving a change in the structure of the ring, as shown in the case of pseudothiohydantoins, have also been observed in the hydantoin series. Diphenylimidohydantoin in the presence of sodium ethylate changes into *unsym* oxalyl diphenylguanidine.[2]

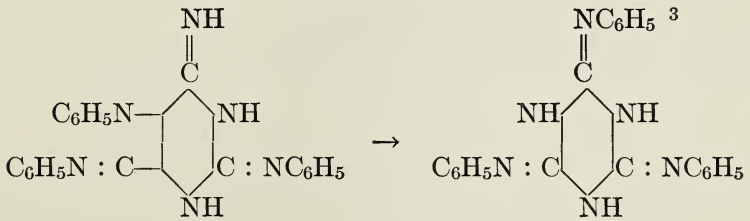


1, 2-Diphenyl-4-imidohydantoin — Oxalyl diphenylguanidine



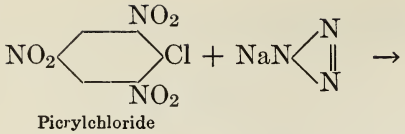
Sym.-Oxalyl diphenylguanidine — *Unsym.*-Oxalyl diphenyl-guanidine

Phenylmelamines also undergo similar molecular changes:

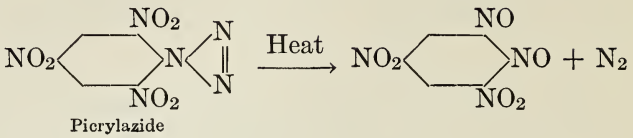


The interesting transformation discovered by Schrader[4] should also be recorded in this series:

[1] Wheeler, Johnson and McFarland, Jour. Am. Chem. Soc., **25**, 787 (1903).
[2] Dieckmann, Ber., **38**, 2980 (1905); Ber., **40**, 3738 (1907).
[3] Rathke, Ber., **20**, 1071 (1887); **21**, 867 (1888).
[4] Ber., **50**, 777 (1917).

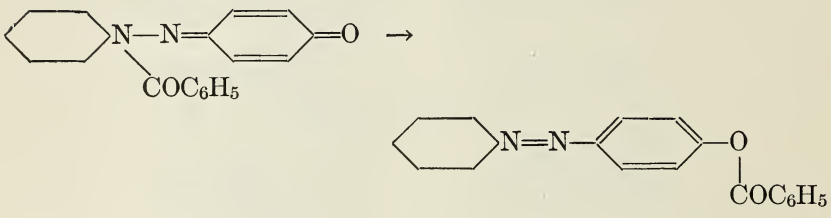


Picrylchloride



Picrylazide

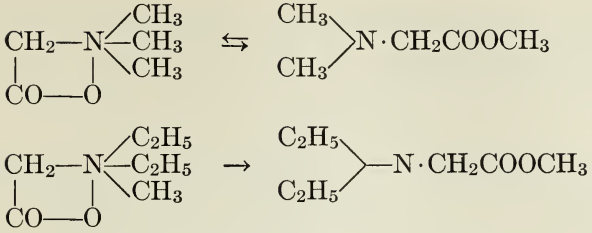
Rearrangements involving the Transference of Radicals from Nitrogen to Oxygen: An illustration of this class is that represented by the transformation of quinone-phenylhydrazone combinations into hydroxy-azo compounds,[1] which was discovered by Willstätter:



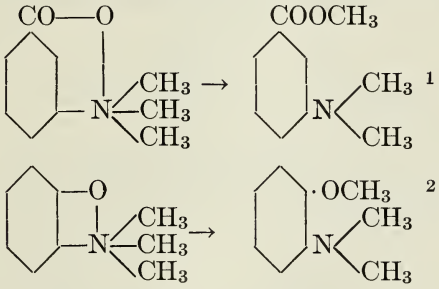
This type of change involves the migration of an acyl group and also takes place when, instead of benzoyl, the acyl radicals $COCH_3$ and $COOC_2H_5$ are in union with the nitrogen.

Betaine rearrangements are to be recorded in this group. Betaine is transformed by heat into the methylester of dimethylamino-acetic acid. The reaction is reversible and is apparently a general one for all α-betaines, although in the case of β-betaines analogous transformations cannot be brought about. Betaine and its isomeric ester—methyl dimethylaminoacetate—are both stable below 135°; between 135° and 293° the betaine is stable and the ester is the unstable modification. Above 293° the betaine cannot exist. In the case of mixed α-betaines containing both ethyl and methyl groups on the nitrogen it is the methyl or smaller radical which migrates from nitrogen to oxygen.[2]

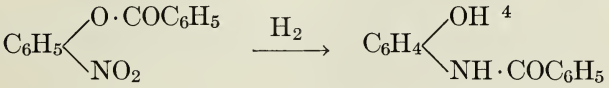
[1] Willstätter and Veraguth, Ber., **40**, 1432 (1907).
[2] Willstätter, Ber., **35**, 587 (1902).



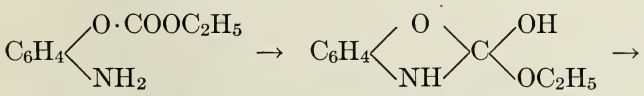
This same type of change has also been observed in the aromatic series:



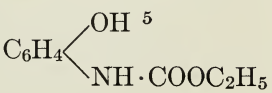
Rearrangements Involving the Transference of Radicals from Oxygen to Nitrogen; one of the first reactions of this kind to be recognized was that described by Böttcher,[3] who found that the benzoyl derivative of *o*-nitrophenol is converted by reduction into benzoylaminophenol:



Ortho-aminophenylcarbonates also undergo a similar transformation; the carbethoxy group migrating to nitrogen. The mechanism of the reaction has not been established, but Ransom assumes the formation of an intermediate addition product as shown below:



Ethyl *o*-aminophenylcarbonate (Not isolated)



[1] Griess, Ber., **6**, 585 (1873).

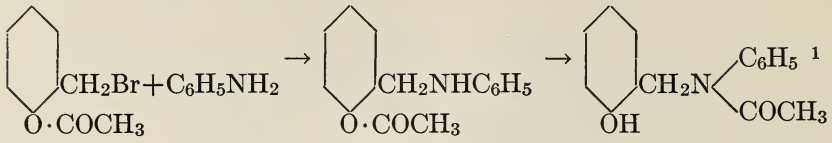
[2] Griess, Ber., **13**, 246 (1880).

[3] Ber., **16**, 630 (1883).

[4] Auwers, Annalen der Chemie, **332**, 159 (1904); Ber., **37**, 2249 (1904); Ber., **33**, 1923 (1900); Einhorn and Pfyl, Annalen der Chemie, **311**, 34 (1900).

[5] Ransom, Am. Chem. Jour., **23**, 11 (1900); Ber., **31**, 1060 (1898); **33**, 199 (1900).

Acyl groups may also migrate from a phenolic oxygen to a nitrogen substituted in a side chain,

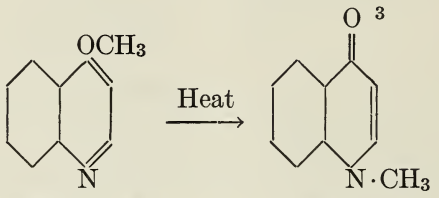


[1]

and Hantzsch assumes that a rearrangement of an acyl group is involved in the formation of *anti*-diazoacetates from diazonium salts,

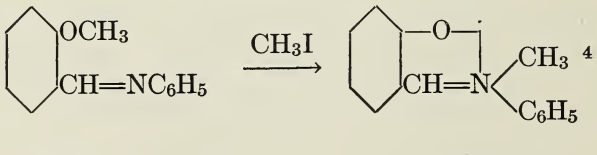
[2]

Rearrangements involving migration of a radical from an oxygen atom substituted in the ring to a nitrogen within the cycle or in a side chain belong in this class:

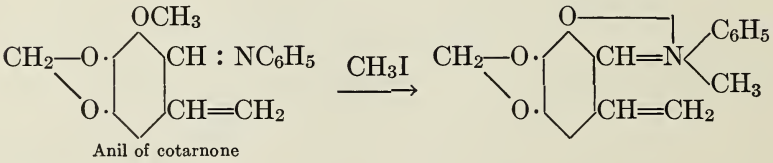


Methoxykynurine — N-Methylkynurine [3]

Analogous changes are brought about in anil combinations by the action of alkyl halides giving amine oxides:



[4]



Anil of cotarnone

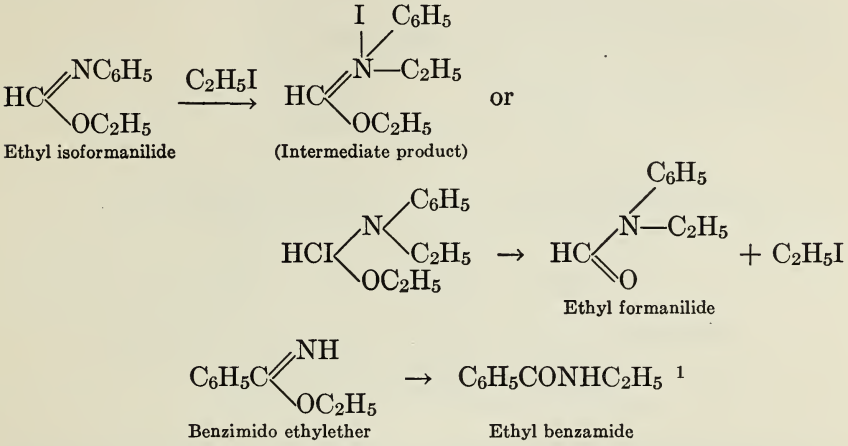
[1] Auwers, Ber., **33**, 1923 (1900).

[2] Hantzsch, and Wechsler, Annalen der Chemie, **325**, 229 (1902).

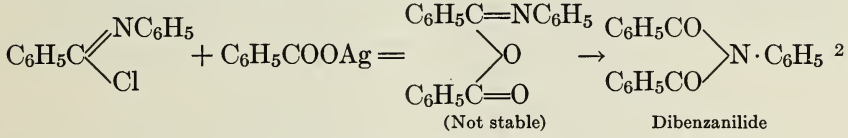
[3] Meyer, Monatsh. Chemie, **27**, 260 (1906); Haitinger and Lieber, Ibid., **6**, 323 (1885); Knorr, Annalen der Chemie, **236**, 104 (1886).

[4] Freund and Becker, Ber., **36**, 1524, 1537 (1903); Brühl, Die Pflanzenalkaloide, pp. 317 (1900).

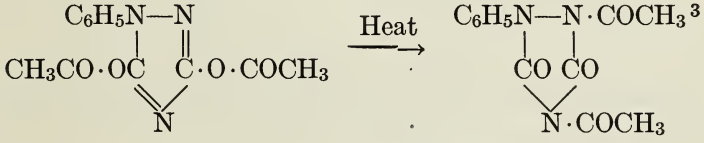
The imidoester rearrangements should be considered at this point. Isomerization of these combinations into acid amides by the action of heat or of alkyl halides has been observed by several investigators,



Imidoacid-anhydride rearrangements may also be included here:



This type of change is also met with in cyclic combinations,

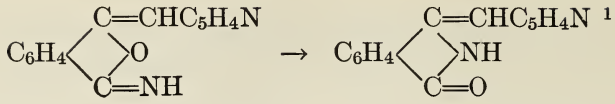


[1] Wheeler and Johnson, Ber., **32**, 35 (1899); Am. Chem. Jour., **21**, 186 (1899); **23** 135 (1900).

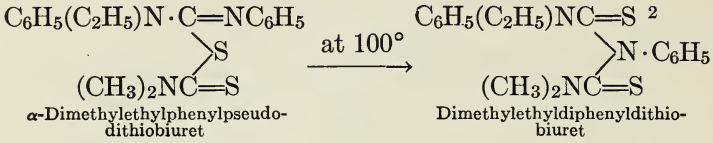
Literature references on imidoester rearrangements: Wislicenus and Goldschmidt, Ber., **33**, 1467 (1900). Hofmann and Olshausen, Ber., **3**, 272 (1870). Hofmann, Ber., 19, 2061 (1886). Meyer and Pinner, "Die Imidoäther und Ihre Derivate," pp. 215. Andreocci, Ber., **24**, R. 205 (1891). Knorr, Ber., **30**, 922, 937 (1897); Annalen der Chemie, **293**, 1 (1896). Wislicenus and Körber, Ber., **35**, 1991, 164 (1902). Gabriel and Neumann, Ber., **25**, 2383 (1892). Lander, Jour. Chem. Soc., **83**, 406 (1903). Meyer and Beer, Monatsh. Chemie, **34**, 1173 (1913).

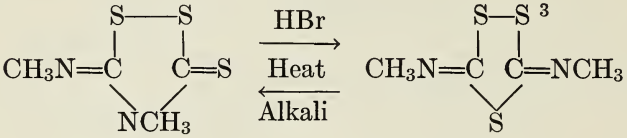
[2] Wheeler and Johnson, Am. Chem. Jour., **30**, 24, 31 (1903).

[3] Hoogewerff and Van Dorp, Rec. trav. chim. des Pay-Bas., **12**, 12 (1893); **13**, 93 (1894). Kuhara and Fukui, Am. Chem. Jour., **26**, 454 (1901); van der Meulen Rec. trav. chim. des Pays-Bas., **15**, 282 (1896).

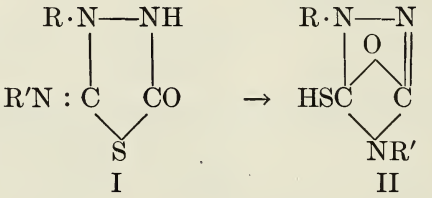


and in thioimido-acid anhydride rearrangements,

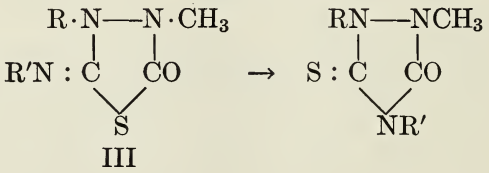




The change of thiodiazoles into triazoles, which was discovered by M. Busch,[4] may now be considered. Thus thiodiazolonanile (I) rearranges in solution, or upon fusion, to give an endoxytriazol-thiol (II):

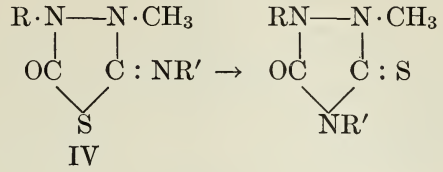


If the hydrogen atom of the imido group in I is replaced by CH_3 the course of the reaction is as follows:



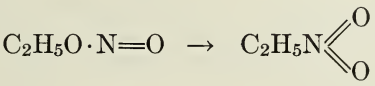
[1] von Huber, Ber., **36**, 1664 (1903).
[2] Billeter, Ber., **26**, 1688 (1893).
[3] Freund, Annalen der Chemie, **285**, 166 (1895).
[4] Busch and Limpach, Ber., **44**, 560 (1911).

Also in the case of substances belonging to a class represented by formula IV and isomeric with III, an analogous rearrangement takes place:

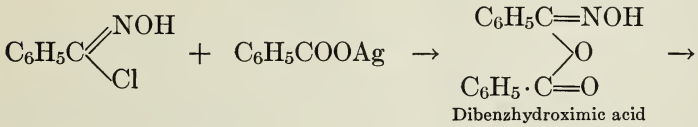


IV

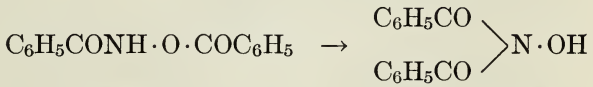
According to Busch and Limpach these transformations of thiodiazole compounds into triazoles are decidedly not reversible processes as Nirdlinger and Acree assume. Aliphatic nitrites can be rearranged to nitro compounds.[1]



Rearrangements Involving the Transference of Radicals from Oxygen to Oxygen; Dibenzhydroximic acids, which are imidoacid-anhydride combinations, rearrange spontaneously to dibenzhydroxamic acids instead of giving diacyl derivatives of hydroxylamine: [2]



Dibenzhydroximic acid



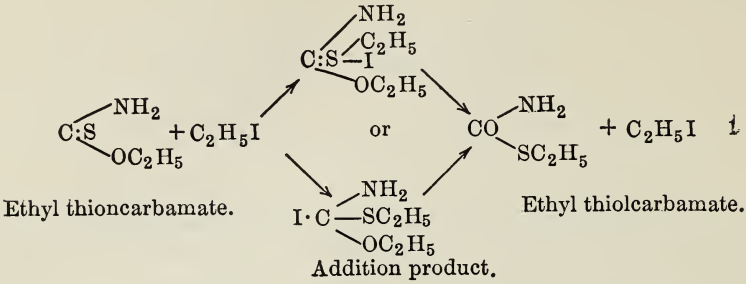
Dibenzhydroxamic acid — Dibenzoyl hydroxylamine

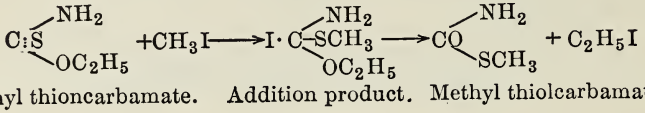
Rearrangements Involving the Transference of Radicals from Oxygen to Sulphur: These molecular transformations are generally brought about by the agency of alkyl halides, and have been investigated very thoroughly by Wheeler and his co-workers. In the presence of alkyl halides thioncarbamates isomerize to give the corresponding thiol combinations, the halide acting in all probability as a catalytic agent. In

[1] Neogi and Chowdhari, Jour. Chem. Soc., **109**, 701 (1916); Gaudion, Annalen chimie et phys., (1912), **25**, 125.

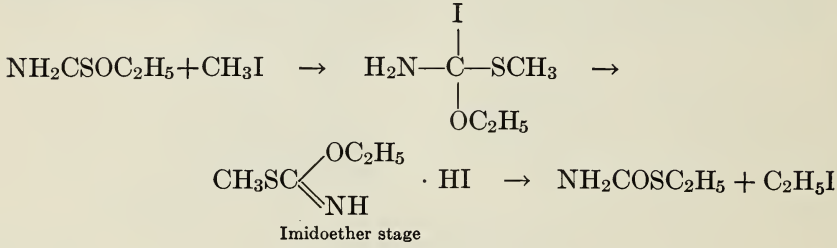
[2] Lossen, Ann. **186**, 42 (1877); Werner and Skiba, Ber., **32**, 1654 (1899). Werner and Buss, Ibid., **27**, 2198 (1894).

the following equations the reaction is interpreted as involving the formation of an intermediate addition product:

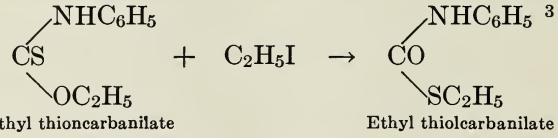




Knoor has recently supported Wheeler's interpretation of this change, but he represents the reaction as taking place in three stages as is represented by the following scheme:[2]



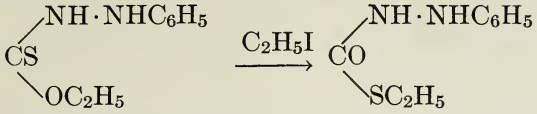
Thioncarbanilates may rearrange to thiolcarbanilates; but the change, however, is not brought about as easily as in the case of the thioncarbamates. Here also alkyl halides act as the catalytic agents:



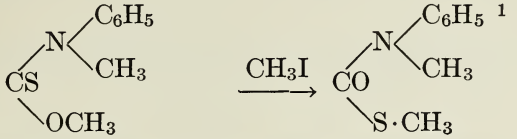
$$R\cdot CSOR' \rightarrow R\cdot COSR'\ ^{4}$$

[1] Wheeler and Barnes, Am. Chem. Jour., **22**, 143 (1899).
[2] Ber., **50**, 767 (1917).
[3] Wheeler and Barnes, Am. Chem. Jour., **24**, 60 (1900).
[4] Bettschart and Bistrzycki, Helv. chim. Acta., **2**, 118 (1919).

Thioncarbazinic esters rearrange to their thiol isomers.

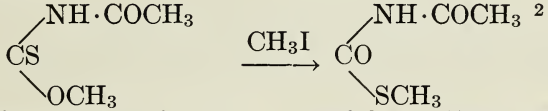


Substituted thioncarbanilates rearrange more easily than the carbanilates themselves.



[1]

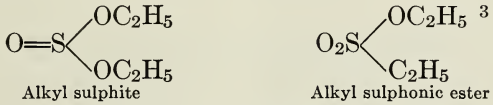
Acylthioncarbamates show little tendency to isomerize to the isomeric thiol combinations.



Methyl acetyl thioncarbamate — Methyl acetyl thiolcarbamate

[2]

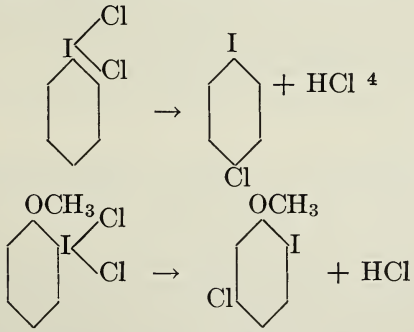
Alkyl sulphites can be isomerized to their isomeric alkyl sulphonic esters.



Alkyl sulphite — Alkyl sulphonic ester

[3]

Rearrangements Involving the Transference of Radicals from Iodine to Carbon: Intramolecular halogenation is illustrated by the transformation of phenyliododichloride into *p*-iodochlorbenzene and of *o*-methoxyphenyliododichloride into 1-methoxy-2-iodo-5-chlorbenzene. These unique changes are accelerated by the action of sunlight:



[4]

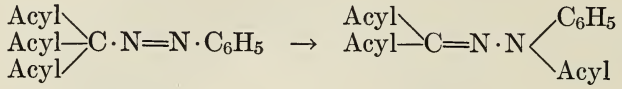
[1] Wheeler and Dustin, Am. Chem. Jour., **24**, 425 (1900).

[2] Wheeler and Johnson, Am. Chem. Jour., **24**, 189 (1900).

[3] Rosenheim and Sarow, Ber., **38**, 1300 (1905).

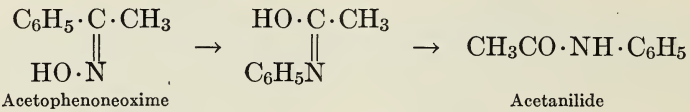
[4] Keppler, Ber., **31**, 1136 (1898); Jannasch, Hinterskirch and Naphtali, Ber., 31, 1710, 1714 (1898).

Rearrangements Involving the Transference of Radicals from Carbon to Nitrogen: A type of change which should be recorded in this series is that involving the rearrangement of azo compounds into hydrazones:



O. Dimroth and Hartmann, who studied this reaction, found that it took place upon heating the dry substance to the fusion temperature or upon warming in indifferent solvents.[1]

The Beckmann Rearrangement. This consists of an interchange of an organic radical and hydroxyl in oxime combinations. A simple illustration is the transformation of acetophenone oxime into acetanilide and may be expressed by the following equation in which the C_6H_5 group is represented as migrating from carbon to nitrogen:



Acetophenoneoxime — Acetanilide

This type of change is very general in both the cylic and acylic series and is brought about by the action of acid dehydrating agents, such as phosphorus pentachloride, organic acid chlorides and anhydrides, acetic acid, sulphuric and hydrochloric acids, and phosphorus pentoxide. The reagent first used by Beckmann to produce the change was phosphorus pentachloride. Although the mechanism of the change has received very careful study by numerous investigators, it is still very obscure. Several theories have been proposed,[2] but none has as yet finally supplanted Beckmann's original interpretation, which is still strongly supported by experimental evidence.

Beckmann[3] assumed that a direct interchange of radicals took

[1] Ber., **40**, 4460 (1907).

[2] Beckmann, Ber., **27**, 300 (1894). Baeyer, Ber., **32**, 3627 (1899). Nef, Annalen der Chemie, **298**, 308 (1897); **318**, 39, 227 (1901). Stieglitz, Am. Chem. Jour., **18**, 751 (1896); **29**, 49 (1903); Ber., **43**, 782 (1910). Slosson, Am. Chem. Jour., **29**, 289 (1903). Werner and Piguet, Ber., **37**, 4295 (1904). Sluiter, Rec. trav. chim. des Pays-Bas, **24**, 372 (1905). Wallach, Annalen der Chemie, **346**, 272 (1906). Diels and Stern, Ber., **40**, 1631 (1907). Schroeter, Ber., **42**, 2136 (1909). Montagne, Rec. trav. chim. des Pays-Bas, **25**, 376 (1906); Ber., **43**, 2014 (1910). Kuhara and Co-workers, Memoirs College Science and Engineering Kyoto Univ. (Japan), 1907–1916. Hantzsch, Ber., **35**, 3579 (1902).

[3] Ber., **19**, 988 (1886); **27**, 300 (1894).

place between carbon and nitrogen, and that the reagent used acted merely as a catalyst. Kuhara, on the other hand, postulated that the action of the acid chloride or anhydride, when these bodies were used as reagents, interacted with formation of an acyl derivative, and that this then rearranged with an interchange of radicals to give imidoacid anhydride combinations as secondary products. These are then broken down by hydrolysis with the formation of the anilide. According to Kuhara, the more negative the acid radical the greater will be the tendency to rearrange. This view is practically identical with Beckmann's first interpretation of the reaction which bears his name,

$$\begin{array}{l} R\cdot C\cdot R' \\ \quad\| \\ \quad N\cdot OH \end{array} \xrightarrow{(CH_3CO)_2O} \begin{array}{l} R\cdot C\cdot R' \\ \quad\| \\ \quad N\cdot O\cdot COCH_3 \end{array} \rightarrow \begin{array}{l} R\cdot C\cdot O\cdot COCH_3 \\ \quad\| \\ \quad N\cdot R' \end{array} \xrightarrow{H_2O} RCO\cdot NHR'$$

$$\begin{array}{l} R\cdot C\cdot R' \\ \quad\| \\ \quad NOH \end{array} \xrightarrow{C_6H_5SO_2Cl} \begin{array}{l} R\cdot C\cdot R' \\ \quad\| \\ \quad N\cdot O\cdot SO_2C_6H_5 \end{array} \rightarrow \begin{array}{l} R\cdot C\cdot O\cdot SO_2R \\ \quad\| \\ \quad NR' \end{array} \rightarrow RCONHR$$

According to the investigations of Wheeler and Johnson[1] imidoacid anhydride combinations corresponding to the acetyl derivative above are unstable compounds and readily rearrange to diacyl anilides. The latter substances would give on hydrolysis the product of rearrangement or the *mono*-acylanilide.

According to Hantzsch and others the transformation of an oxime to an anilide by the action of phosphorus pentachloride is to be represented as follows:

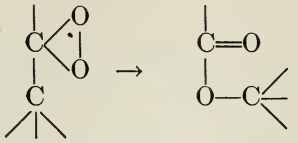
$$\begin{array}{l} C_6H_5\cdot C\cdot C_6H_5 \\ \quad\| \\ \quad N\cdot OH \end{array} \xrightarrow{PCl_5} \begin{array}{l} C_6H_5\cdot C\cdot C_6H_5 \\ \quad\| \\ \quad N\cdot Cl \end{array} \rightarrow \begin{array}{l} C_6H_5C\cdot Cl \\ \quad\| \\ \quad N\cdot C_6H_5 \end{array} \xrightarrow{H_2O}$$

Stieglitz and Peterson,[2] who later synthesized several chlorimido compounds of this type, were unable to effect a rearrangement of such combinations.

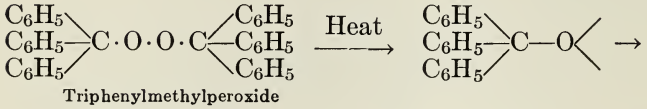
[1] Am. Chem. Jour., **30**, 24, 31 (1903).

[2] Ber., **41**, 782 (1910); Am. Chem. Jour., **46**, 325 (1911).

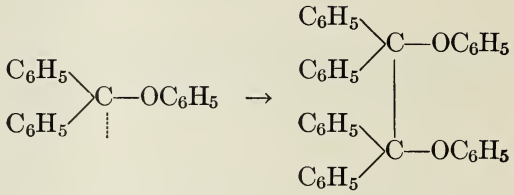
The rearrangement of ketonic oxides into acid esters recently discovered by A. von Baeyer and Villiger,[1] has been interpreted by them as analogous to the Beckmann rearrangement:



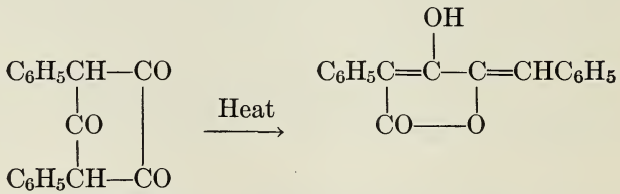
Wieland's interesting peroxide rearrangement may be recorded here:[2]



Triphenylmethylperoxide



An interesting rearrangement, the mechanism of which is not understood and which was originally described by Claisen,[3] is that of oxalyl dibenzylketone into an isomeric lactone combination:



Oxalyl dibenzylketone

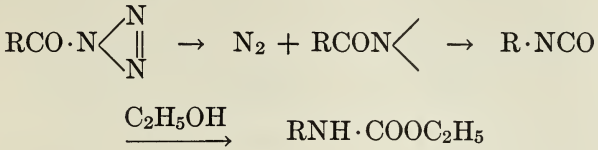
Stieglitz considers that three important rearrangements may be arranged in the same general group and are therefore capable of much

[1] Ber., **32**, 3625 (1899).

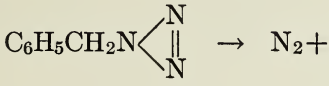
[2] Ber., **44**, 2550 (1911).

[3] Claisen and Ewan, Annalen des Chemie, **284**, 290 (1895); Bamberger, Jour. prakt. Chemie, **51**, 588 (1895).

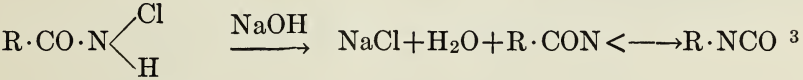
the same interpretation. These are the Hofmann rearrangement, the Curtius process of passing from acylazides to urethanes and

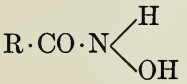


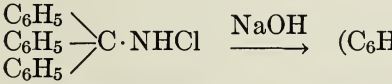
from alkylazides to imides; and the



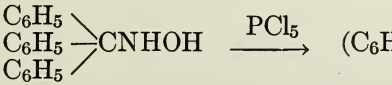
Beckmann change. In order to develop a general explanation of the mechanism of these transformations he supposes that in all such cases the transformation results from the formation of univalent nitrogen derivatives or unsaturated radicals as intermediate products, and assumes further that the free valences of the univalent nitrogen are powerful enough to detach the radical R from carbon and bring about a rearrangement to a stable molecule. In other words, the presence of univalent nitrogen in the intermediate compounds is assumed to be responsible for all rearrangements in this entire group.[2]







Triphenylmethylchloramine Phenylimidobenzophenone



[1] Curtius, Jour. prakt. Chemie, **63**, 428 (1901); Ber., **35**, 3229 (1902).

[2] Stieglitz and Leech, Jour. Am. Chem. Soc., **36**, 272 (1914); Stieglitz, Ber., **43**, 782 (1910); **46**, 2149 (1913); Am. Chem. Jour., **46**, 327 (1911).

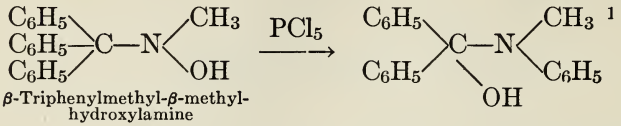
[3] Stieglitz and Leech, Jour. Am. Chem. Soc., **36**, 272 (1914).

[4] Lossen, Annalen der Chemie, **161**, 359 (1872).

[5] Stieglitz and Vosburgh, Ber., **46**, 2151 (1913); Jour. Am. Chem. Soc., **38**, 2081 (1916).

[6] Stieglitz and Leech, Ber., **46**, 2147 (1913); Jour. Am. Chem. Soc., **36**, 272 (1914).

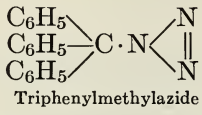
In reviewing the various types of change classified together under Hofmann's rearrangement, it is obvious that a univalent nitrogen derivative cannot be formed when an oxime of the type of β-triphenylmethyl-β-methylhydroxylamine undergoes rearrangement:



β-Triphenylmethyl-β-methylhydroxylamine

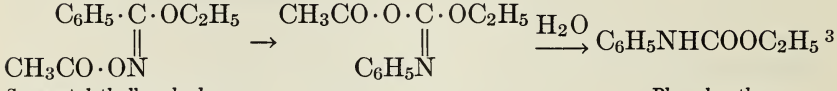
[1]

Whether we are dealing here with a mechanism other than a direct interchange of radicals as postulated by Beckmann remains to be established:



Triphenylmethylazide

Heat → $(C_6H_5)_2C:NC_6H_5+N_2$ [2]

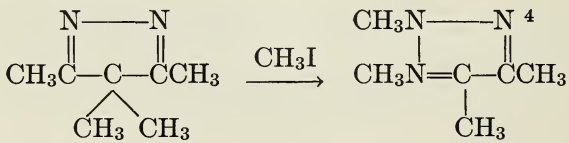


Syn-acetylethylbenzhydroximic ester

Phenylurethane.

[3]

An interesting rearrangement brought about by the catalytic action of methyliodide is that of 3,4,4,5-tetramethylpyrazol into 1,3,4,5-tetramethylpyrazol.



[4]

Rearrangements which are accompanied by an Elimination of Groups of Atoms: The decompositions of diazonium compounds and the Sandmeyer [5] reaction may be regarded as instances of rearrangements belonging in this series:

$$C_6H_5N_2OH \rightarrow N_2 + C_6H_5OH$$

$$C_6H_5N_2Cl(Br) \rightarrow N_2 + C_6H_5Cl(Br)$$

$$C_6H_5N_2(CN) \rightarrow N_2 + C_6H_5CN, \text{ etc.}$$

[1] Stieglitz and Stagner, Jour. Am. Chem. Soc., **38**, 2049 (1916).

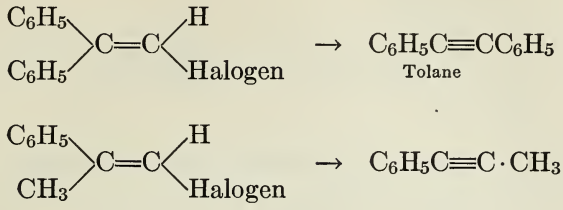
[2] Senior, Jour. Am. Chem. Soc., **38**, 2718 (1916).

[3] Kuhara, Jour. Chem. Soc., **106**, 538 (1914).

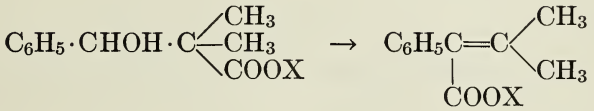
[4] Oettinger, Annalen der Chemie, **279**, 247 (1894).

[5] Griess, Annalen der Chemie, **137**, 67 (1866); Sandmeyer, Ber., **17**, 1633, 2650 (1884); **23**, 1880 (1890).

as may, also, the transformation of unsymmetrical monohalogen-ethylene derivatives into tolanes: [1]



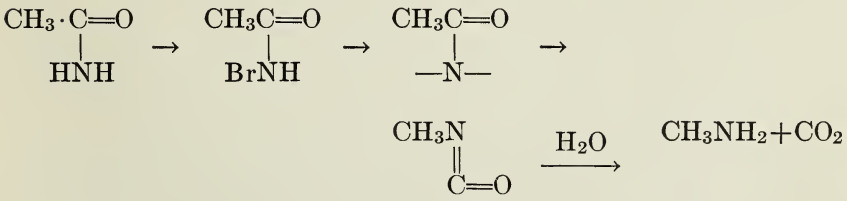
and the transformation of phenylhydroxypivallic acid esters into esters of α-phenyl -β, β-dimethylacrylic acid: [2]



The conversion of acid amides into amines by the action of bromine in alkaline solution belongs to this same group of rearrangements and was discovered by A. W. Hofmann: [3]

$$R \cdot CONH_2 \rightarrow RNH_2$$

The course of the change is explained as follows: [4]



[1] Annalen der Chemie, **279**, 328, 335 (1894); Tiffeneau, Compt. rend., **135**, 1348 (1902).

[2] Tiffeneau, Rev. gén. Sci. pur. et appli. (1907), p. 587.

[3] Ber., **15**, 762 (1882).

[4] Hoogewerff and van Dorp, Rec. trav. chim. des Pays-Bas, **15**, 107 (1896); Stieglitz, Am. Chem. Jour., **18**, 752 (1896); Graebe, Ber., **35**, 2747 (1902); Hantzsch, Ber., **35**, 3579 (1902); Lapworth, Proc. Chem. Soc., **19**, 22 (1903); Mohr, Jour., prakt. Chemie, **72**, 297 (1905); Schroeter, Ber., **42**, 2337, 3356 (1909); **44**, 1201 (1911).

The transformation of oximes into acid amides, which was discovered by E. Beckmann,[1] and which has already been referred to, is analogous to the preceding:

$$\begin{matrix} R \\ \\ R' \end{matrix}\!\!>\!C{=}NOH \;\rightarrow\; RCONHR'$$

The reaction takes place most readily under the influence of acid reagents, and plays an important rôle in the determination of the constitution of stereoisomeric nitrogen compounds. At present it is regarded as a special case of the Hofmann rearrangement, which will be discussed more fully at the end of this chapter.

When these various reactions involving molecular rearrangements are considered merely with reference to the results obtained, it is apparent that in all cases an interchange of atoms or groups of atoms takes place, and that this is accompanied by a more or less pronounced change in molecular constitution, often resulting in the elimination of H_2O, HCl, N_2, etc. Frequently the course of such transformations is represented in the simplest empirical and mechanical manner, and the facts are described without any attempt to explain them. For example, in the case of the rearrangement of phenylhydroxylamine into *p*-amidophenol:

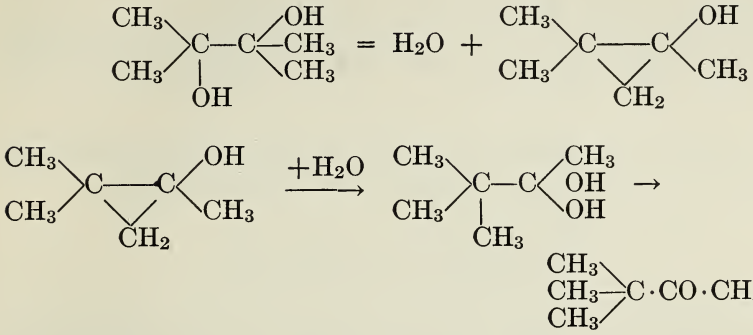
$$C_6H_5NHOH \;\rightarrow\; HOC_6H_4\cdot NH_2$$

the statement is made that the hydroxyl group changes place with the hydrogen atom occupying the *p*-position in the benzene nucleus. At other times, however, and this is especially true in the case of those rearrangements involving complicated molecular changes, explanations are attempted in an effort to avoid the assumption of such sudden and direct interchanges of groups of atoms and the theory is advanced that intermediate products are formed in the course of all such transformations. The fate of many explanations of this kind is illustrated in the case of the pinacoline rearrangement. E. Erlenmeyer, Sr.,[2] considered it probable that in this transformation water was split off and a trimethylene derivative formed. Since water was added again at

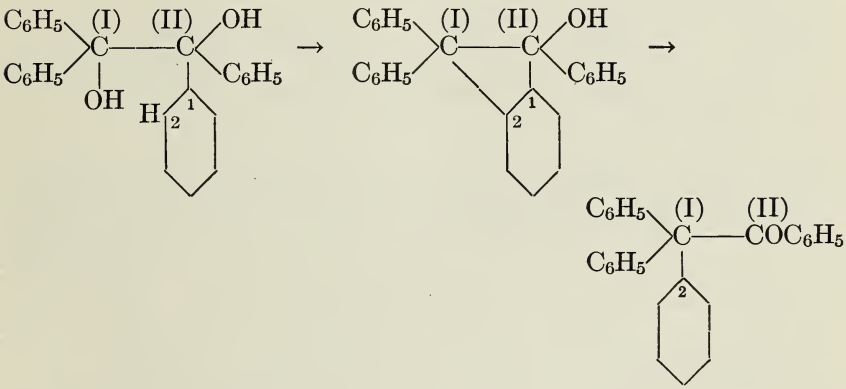
[1] Ber., **19**, 988 (1886); **20**, 1507, 2580 (1887); **21**, 766 (1888); Annalen der Chemie, **252**, 1 (1889); Ber., **27**, 300 (1894); Stieglitz, Am. Chem. Jour., **18**, 751 (1896); **29**, 49 (1903); Nef, Annalen der Chemie, **318**, 227 (1901); Slosson, Am. Chem. Jour., **29**, 289 (1903); Werner, Ber., **37**, 4295 (1904); Sluiter, Rec. Trav. chim. des Pays-Bas., **24**, 372 (1905); Wallach, Annalen der Chemie, **346**, 272 (1906); O. Diels and Stern, Ber., **40**, 1631 (1907).

[2] Ber., **14**, 322 (1881).

another point the rearrangement could be interpreted structurally in the following manner:



Since, now, tetraphenyl pinacone rearranges to a corresponding pinacoline, the mechanism of this reaction must be the following, if the above interpretation is right in principle:

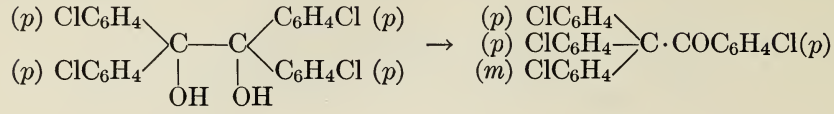


It is obvious that in this process of condensation the benzene nucleus, which was originally bound to the carbon atom II by its valence 1, becomes ultimately attached to the carbon atom I by its valence 2, or at least by some valence other than its valence 1. In other words, a change in the point of union of one of the benzene rings must take place if this is the mechanism of the reaction.

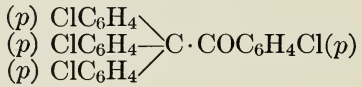
Since it has not been possible to isolate the intermediate products of this change, Montagne [1] devised a means for proving experimentally the course of the rearrangement in the case of *p*-tetrachlorphenyl-pinacone. If Erlenmeyer's interpretation is correct this substance

[1] Rec. trav. chim. des Pays-Bas, **24**, 105 (1905); **25**, 413 (1906).

should pass into a pinacoline in which one of the chlorine atoms occupies not the *para*-position but the *meta*-position in the ring.

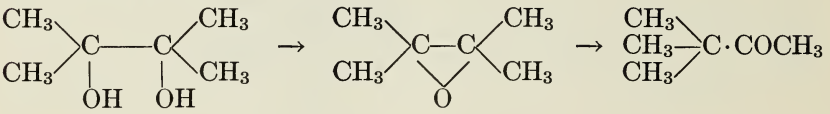


This, however, was found not to be the case as the resulting pinacoline was shown to have all four chlorine atoms in the *para*-position.

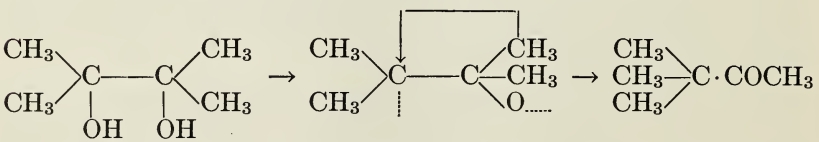


This discovery was verified later by Acree, and thus Erlenmeyer's whole scheme became in the highest degree improbable.

Other investigators [1] have postulated that an oxide or cyclic ether is formed in the process of the rearrangement which is isomeric with the resulting ketone or pinacoline.



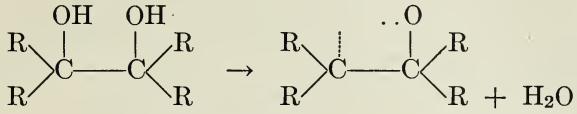
Since, however, organic oxides are relatively stable in the presence of dehydrating agents, Montagne and Meerwein came to the conclusion that characteristic intermediate products were not formed, and that the pinacoline conversion represents a genuine case of intramolecular rearrangement accompanied by the elimination of water. The question then arose as to whether the loss of water takes place before or after the rearrangement. Tiffeneau,[2] after studying the reaction, was of the opinion that the interchange of groups took place as a result of the action of the hydrating agents; and he gives an expression for the reaction which implies only these facts. This explanation assumes the intermediate formation of trivalent carbon combinations.



[1] Erlenmeyer, Jr., Annalen der Chemie, **316**, 84 (1901); Nef, Annalen der Chemie, **335**, 243 (1904).

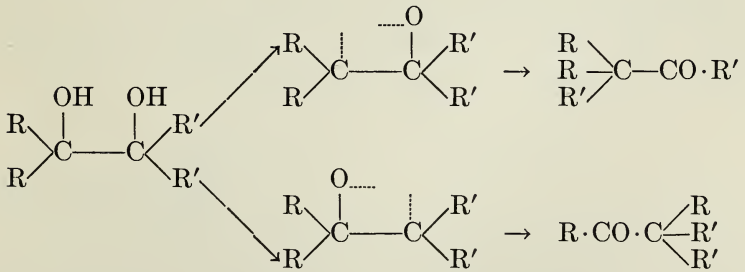
[2] Revue gen. Sci. pur. et appli., 1907, 591.

It seems to have been established conclusively by the work of Montagne [1] and Meerwein [2] that ethylene oxide or trimethylene combinations are not intermediate products in pinacoline rearrangements. According to their interpretation the first stage of these transformations involves a loss of water with formation of an unsaturated combination as is represented below:



A condition of stability is then established in the unsaturated radical by migration of one of the groups R from carbon to carbon with formation of a ketone. If R represents a cyclic group this becomes linked in the ketone by the same carbon atom of the cycle, which served to hold the grouping in its original position in the glycol.[3]

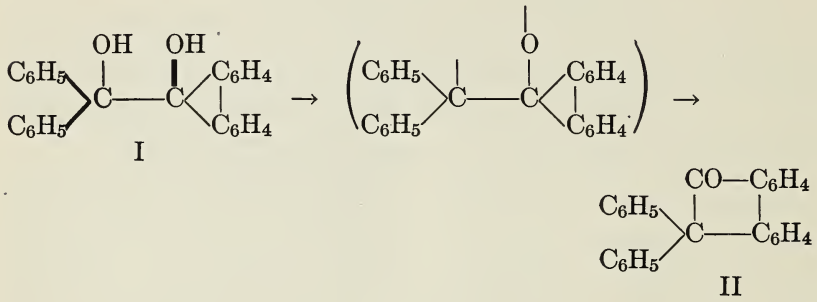
In his study of the mechanism of these rearrangements Meerwein [4] has revealed some very interesting and important data regarding the intensity of molecular attraction or affinity of atoms and radicals in glycol combinations. For example, in the splitting off of water, he assumes that the most loosely bound hydroxyl and hydrogen atom function in this change; and that the reactivity of the hydroxyl group is dependent directly upon the nature of the respective radicals joined to the same carbon atom in the glycol. Interesting relations were brought out by a study of the rearrangements of unsymmetrical pinacone combinations:



The introduction of a benzene radical into a glycol increased strongly the reactivity of the adjoining hydroxyl group or, in other words, this

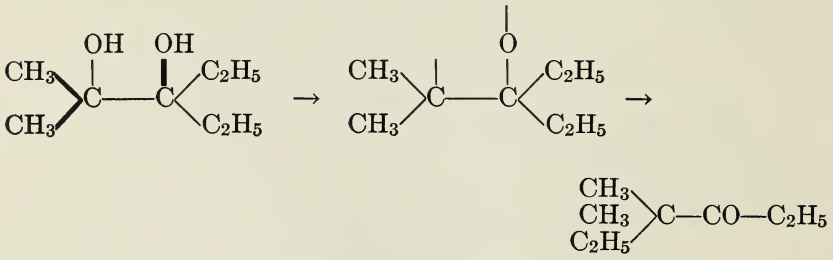
[1] Rev. génér. (1907), 591.
[2] Annalen der Chemie, **396**, 200 (1913).
[3] Montagne, Ber., **51**, 1482 (1918).
[4] Annalen der Chemie, **419**, 921 (1919).

cycle neutralized, so to speak, a larger proportion of the valency of the glycol carbon. This results in a loose combination of hydroxyl and consequently an increased tendency for this group to split off and form water. A study of molecular rearrangements in glycol combinations containing phenyl and phenylene radicals led to the interesting result that the phenyl radical absorbs a greater proportion of the carbon valency in the glycol than a phenylene radical, and consequently renders more reactive its adjoining hydroxyl group. He found, for example that *asym*-diphenyl-phenylene-glycol I undergoes a rearrangement to 9, 9-diphenyl-phenanthrone II as is represented below:



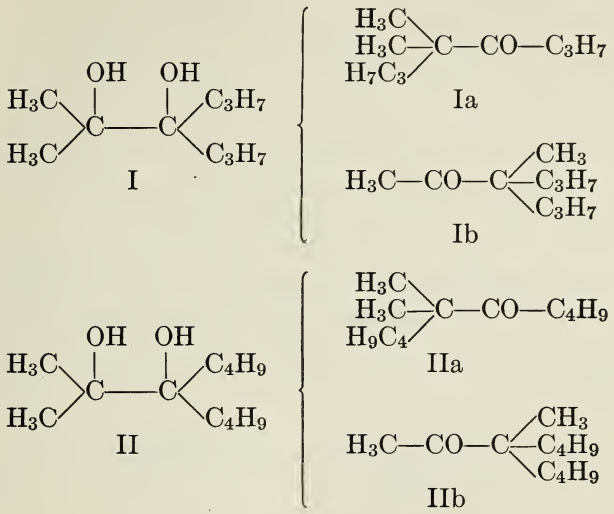
I II

In aliphatic combinations a methyl radical neutralizes or absorbs more valency energy than an ethyl group. For example, dimethyl diethyl-glycol rearranges to ethyl amylketone:



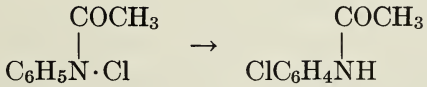
Dimethyl di-normalpropyl-glycol and dimethyl di-normalbutyl glycol rearrange to give mixed ketones, and an analysis of the products of reaction revealed the interesting fact that a methyl and *n*-propyl group neutralize about an equal amount of affinity of a carbon atom in glycol combinations. The ability of radicals to neutralize affinity is not constant and directly proportional to the size or molecular magnitude of the respective radicals but changes periodically, and *n*-alkyl

groups containing an uneven number of carbon atoms absorb more affinity than those containing an even number of carbon atoms:



In both the pinacone and the Beckmann rearrangement a phenyl group always attaches itself after migration through a common carbon atom. For example, *p*, *p*-dichlorobenzophenone oxime rearranges smoothly to *p*-chlorbenzoyl-*p*-chloranilide.[1]

Reactions which involve the shifting of atoms and radicals from a side chain of the benzene ring into the nucleus are of special importance to an understanding of the processes of substitution in the benzene ring. In considering, for example, the change of N-chloracetanilide into *p*-chloracetanilide:



it may be supposed either that one molecule acts as a chlorinating agent with reference to a second, or that there is simply an exchange of a chlorine for a hydrogen atom inside one and the same molecule. In the first case the change belongs to the order of bi- or polymolecular reactions. Blanksma actually found by following the rate of reaction experimentally that it was monomolecular. Reasoning by analogy, other migrations of atoms and groups from the side chain into the benzene nucleus might be regarded as exchanges taking place within

[1] Montagne, Ber., **51**, 1479 (1918).

a single molecule. Certainly the splitting off of certain substituents of side chains have been observed frequently. In the rearrangement of phenylnitramine into *o*- and *p*-nitroanilines, for example, the presence of nitrous acid has been demonstrated often, though in such small quantities as to be almost negligible as far as theoretical considerations are concerned. E. Bamberger, who made the observation,[1] says in regard to it: "it is not strange, in view of the great amount of chemical energy which is stored up in phenylnitramine, that a small part of its nitrogen should separate in the form of nitrous acid, even if it were not present originally in the form of nitroso groups."

Hantzsch, in cooperation with his students Schleissing and Jäger, has shown, by a study of diazo-compounds, that brominated benzene diazonium chlorides, rearrange readily into chlorinated benzene diazonium bromides. This rearrangement has already been referred to in this chapter:

$$\begin{array}{ccc} Br_3C_6H_2\underset{\underset{N}{|||}}{N}\cdot Cl & \rightarrow & ClBr_2C_6H_2\underset{\underset{N}{|||}}{N}\cdot Br \end{array}$$

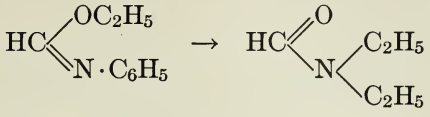
"The conditions under which this very remarkable [2] rearrangement takes place are the following: the tendency to rearrangement increases with the increase in the number of bromine atoms present in the benzene ring. Only bromine atoms in the *o*- and *p*-, never those in the *m*-position may be exchanged for chlorine. The change takes place very rapidly in mixed solutions of ether and alcohol and only slowly in aqueous solutions. It is slightly accelerated by the presence of free hydrochloric acid, and very greatly accelerated by an elevation in temperature."

Now it was conceivable that this transformation took place by the action of one molecule upon another, and belonged, therefore, to the order of bimolecular reactions. The rate of reaction in methyl alcohol measured by Hantzsch and Symthe, gave, however, a constant, agreeing not with the calculated for a bimolecular, but for a mono-molecular reaction. This, also, must be regarded, therefore, as an intramolecular change or one which takes place within a single molecule.

Cases are known, however, where rearrangements take place which involve the formation of intermediate products and where, under favorable conditions these intermediate products may be isolated. The transformation of imidoethers into acid amides will serve as an illus-

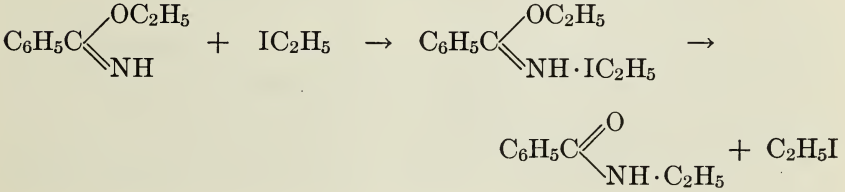
[1] Ber., **30**, 1248 (1897).
[2] Ber., **33**, 505 (1900).

tration. According to W. Wislicenus this reaction takes place in some cases more or less easily upon heating.[1]

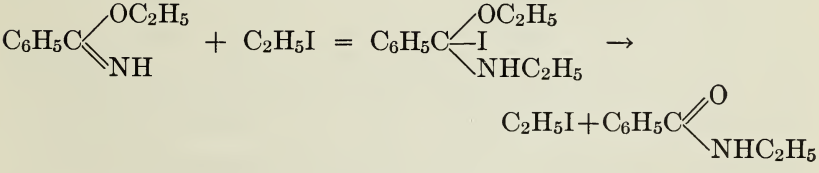


And Wheeler and Johnson [2] found that certain representives of monosubstituted imidoether combinations go over into substituted acid amides in the presence of ethyl or methyliodide at a temperature below 100°. In this case it is necessary to assume one of two courses for the reaction. The alkyl halide first adds to form an intermediate product which may have theoretically two formulas depending upon the manner of addition:

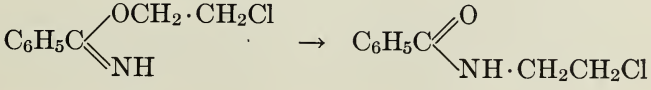
(1) Addition with formation of a pentavalent nitrogen derivative:



(2) Addition to both carbon and nitrogen with saturation of the double bond in the imidoester:

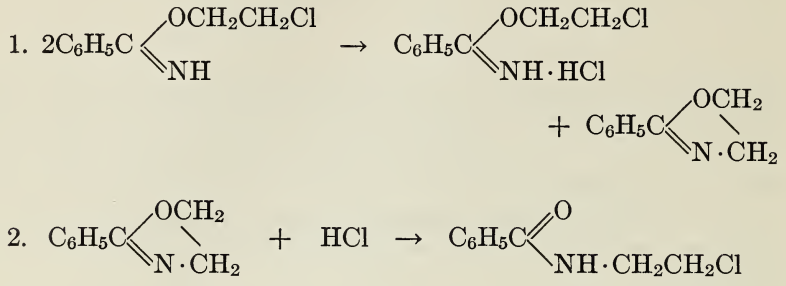


The rearrangement of benzimido-β-chlorethyl ester into β-chlorethylbenzamide takes place in a manner analogous to the interpretation of Wheeler and Johnson, and has been formulated by Gabriel and Neumann [3] as follows:



[1] Ber., **33**, 1467 (1900).
[2] Ber., **32**, 41 (1899); Am. Chem. Jour., **21**, 185 (1899); **23**, 140 (1900).
[3] Ber., **25**, 2386 (1892).

Wislicenus [1] has since demonstrated that this change takes place in the sense of Wheeler and Johnson's interpretation, or by means of so-called intramolecular alkylation, and was able to isolate the intermediate product:



It is obvious from this and other transformations that there are several possible ways according to which rearrangements may take place; and it becomes necessary to inquire into each individual case as to whether a genuine intramolecular exchange of atoms or groups of atoms has occurred, or whether an interaction has taken place between molecules. In answering this question physico-chemical methods are of the greatest importance in supplementing purely chemical investigation.

It is far from easy to explain satisfactorily at the present time, in terms of structural chemistry, the mechanism of such rearrangements as take place entirely within an organic molecule, especially when the intermediate products cannot be isolated. In such cases violent and sudden displacements both of atoms and of organic radicals seem to occur. Some investigators believe that a direct dissociation of unsaturated radicals from the molecule is the only assumption left open in explaining these changes, and Nef's theories consequently have found frequent application in such cases though in a somewhat modified form.[2]

Rearrangements of this type are often represented as resulting from the mobility of the atoms inside the molecule, and assumptions are made regarding the form and movements of certain atoms. Thus the system of atoms in a compound capable of undergoing rearrangement, may be imagined as being in a condition of mobile equilibrium between two or more stable phases. In the course of a series of changes molecular aggre-

[1] Ber., **35**, 164, 1991 (1902).

[2] Nef, Annalen der Chemie, **298**, 307 (1897); **318**, 137 (1901); Jour. Am. Chem. Soc., **26**, 1564 (1904); J. von Braun, Ber., **38** (1905), **44** (1911).

gates are passed through which are not capable of existing as chemical compounds. A. Lapworth,[1] more than any other, has succeeded in representing the phenomena of rearrangements in general terms, that are in harmony with the prevailing conceptions in regard to the carbon atom. His elaborations, which have faults common to all explanations which are based upon the conception of the mobility of the atoms, may be summarized briefly. Lapworth [2] points out, in connection with Armstrong's [3] theoretical deductions, that molecular rearrangements (inclusive of tautomerism and desmotropism) take place only in the case of certain well defined groupings of the atoms. Of these groups atoms, two may be considered first, because they stand out as pre-eminent in the tendency of each to pass readily into the other, i.e.,

$$\begin{array}{ccccc} E_1\cdot E_2 : E_3 & \rightleftarrows & E_1 : E_2\cdot E\cdot_3 \\ | & & & & | \\ R_1 & & \text{I} & & R' \end{array}$$

where E_1, E_2, E_3, signify elements as C, N, O, S, etc., and R_1, R_2, etc., organic substituents bound to these elements.

If now, as is usually the case, a mobile atom or radical R_2 as for example, a hydrogen atom, is bound to E_3, the scheme represented in I assumes the following form:

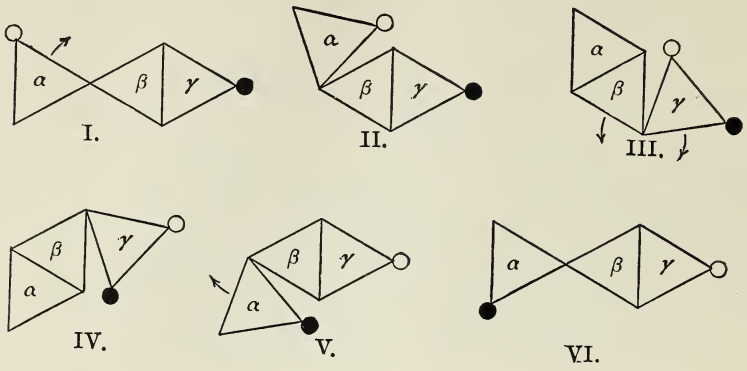
$$\begin{array}{ccccccc} E_1\cdot E_2 : E_3 & \rightleftarrows & E_1 : E_2E_3 & \rightleftarrows & E_1E_2 : E_3 \\ | \quad | & & \diagup \quad \diagdown & & | \quad | \\ R_1 \quad R_2 & & \text{II} \quad R_1 \quad R_2 & & R_2 \quad R_1 \end{array}$$

This rearrangement may proceed in one direction quite as readily as in the other, and in the case of tautomeric substances generally operates in both ways.

Lapworth [4] represents the mechanism of this process in the special case $E_1{=}E_2{=}E_3{=}C$ by means of a diagram. In this scheme the carbon atoms are assumed to lie at the centers of tetrahedra, and the complete molecule is imagined as projected upon the plane of the paper in such a manner that the characteristic unions lie in this plane. Under these circumstances only the upper surfaces of the tetrahedra are shown, the incidence of two sides signifying a union by means of double bonds, and the incidence of two corners, a union by means of single bonds.

[1] Jour. Chem. Soc., **73**, 445 (1898).
[2] Jour. Chem. Soc., **73**, 446 (1898).
[3] Jour. Chem. Soc., **51**, 258 (1887).
[4] Jour. Chem. Soc., **73**, 445 (1898).

The following figure applies to the second equation, II, arrows indicating the direction in which the atoms move:



It is not necessary to assume that the labile groups, R, and R_2 (represented in the diagram by ○ and ●), are in reality free groups; but rather that each is at all times under the influence of the specific attraction of C_1, or C_2, while coming at given moments within the spheres of attraction of both of these carbon atoms.

If such a process is reversible, we have the phenomenon of tautomerism; if it has a definite tendency to proceed in either one direction we have the phenomenon of intramolecular rearrangement (including desmotropism). The process may be only partially, or wholly complete. The following reactions adapt themselves to this scheme:

$$E_1 \cdot E_2 : E_3 \rightleftarrows E_1 : E_2 \cdot E_3$$

$$(R)HS \cdot C \vdots N \rightarrow S : C : NH(R)$$

Thiocyanic acid and derivatives — Isothiocyanic acid and derivatives

$$(R)HO \cdot C \vdots N \rightarrow O : C : NH(R)$$

Cyanic acid — Isocyanic acid

$$HN : C : NH \rightleftarrows N{\equiv}C \cdot NHH$$

Carbodiimide — Cyanamide, etc.

$$HO \cdot C{\equiv}N \rightleftarrows O : C : NH$$

Lactim — Lactam

$$H\ddot{C} \cdot N : O \rightleftarrows C : N \cdot OH$$

Nitroso — Isonitroso

$$H\ddot{C} \cdot \underset{\underset{O}{\|}}{N} : O \rightleftarrows C : \underset{\underset{O}{\|}}{N} \cdot OH$$

Nitro — Isonitro

$$E_1 \cdot E_2 : E_3 \rightleftarrows E_1 : E_2 \cdot E_3$$

$$HO\cdot C(CH_3) : CH\cdot COOC_2H_5 \rightleftarrows O : C(CH_3)\cdot CHH\cdot COOC_2H_5$$

Esters of 2-hydroxycrotonic acid — Acetoacetic acid esters

$$E_1\cdot E_2 : E_3 \rightarrow E_1 : E_2\cdot E_3$$

$$C_2H_5O\cdot C : CH_2 \rightarrow O : C\cdot CH_2\cdot C_2H_5$$

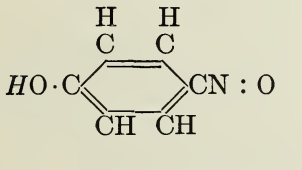
If, now, other unsaturated groups, as $E_4 : E_5$, are joined to the chain $R\cdot E_1\cdot E_2 : E_3$ at the point E_3, analogous oscillations of the tetrahedra give rise to the rearrangements:

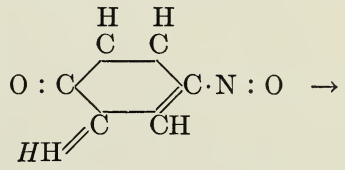
$$E_1\cdot E_2 : E_3\cdot E_4 : E_5 \rightleftarrows E_1 : E_2\cdot E_3\cdot E_4 : E_5 \rightleftarrows E_1 : E_2\cdot E_3 : E_4\cdot E_5$$

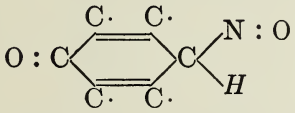
(R) (R) (R)

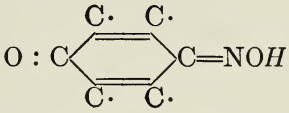
III

The following reactions adapt themselves to this scheme:

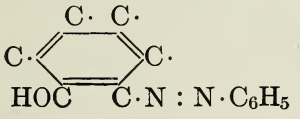


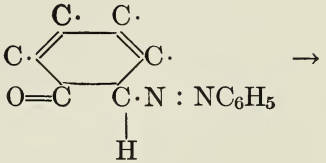


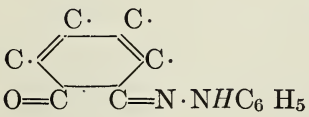




and







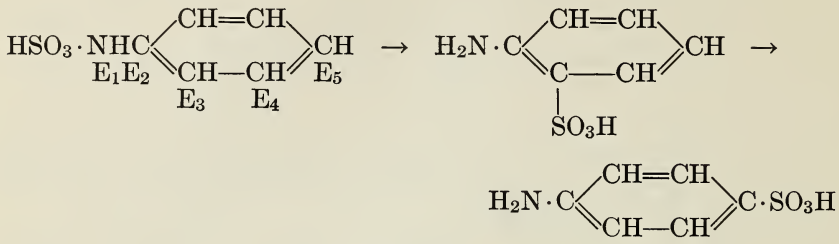
In those cases where hydrogen atoms, or other labile substituents, are in union with E_3 and E_5 rearrangements of the system may be represented thus:

$$E_1\cdot E_2 : E_3\cdot E_4 : E_5 \rightleftarrows E_1\cdot E_2 : E_3\cdot E_4 : E_5 \rightleftarrows E_1\cdot E_2 : E_3\cdot E_4 : E_5$$

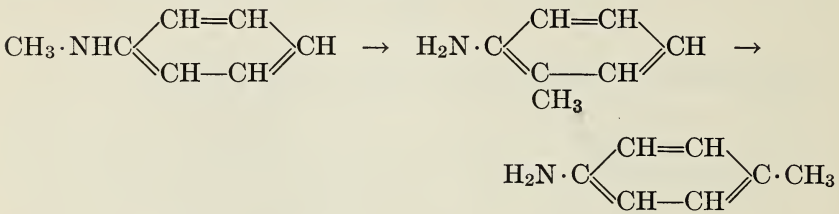
(R_1) (R_2) (R_3) (R_2) (R_1) (R_3) (R_2) (R_3) (R_1)

IV

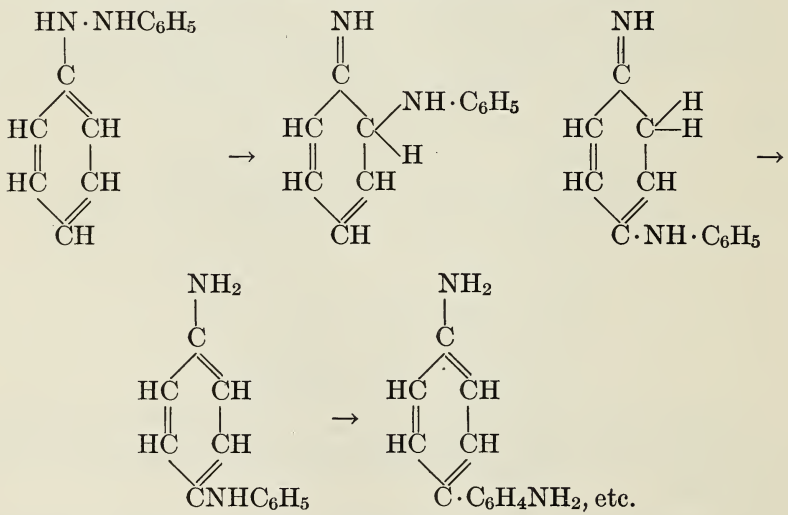
Rearrangements of this type are especially conspicuous among the derivatives of benzene; and all reactions analogous to the sulphonation, nitration, etc., of aniline adapt themselves to this scheme:



also the formation of toluidines from monomethylaniline:



and, further, the semidene and benzidine rearrangements:



Having explained the formation of *o*- and *p*-derivatives of benzene by means of a general scheme, Lapworth next sought to interpret substitution in the *m*-position. To this, and to those cases of rearrange-

ment which involve the elimination of a simple molecule from the complex, it is impossible to do more than to refer in passing.

Views in regard to the mechanism of intramolecular rearrangements which depend upon the ability of multivalent atoms to change their position inside the molecule, have also been developed by E. Erlenmeyer, Junior.[1]

Recently M. Tiffeneau,[2] in a treatise well worth reading, has considered those rearrangements which may be regarded as genuinely intramolecular in character. He divides them into two large groups, comprising, first, those rearrangements which are complete in themselves without addition or elimination of atomic complexes and where the product of the reaction has the same per cent composition as the original substance, as for example, the rearrangement of phenylhydroxylamine into amidophenol, and of phenyl sulphaminic acid into sulphanilic acid. According to Tiffeneau the mechanism of reactions of this type consists first in the cleavage of certain atomic linkages, followed by a reorganization of the molecular structure which results in a change in the relative position of atoms or groups of atoms.

In the second group are included all rearrangements which involve the elimination of hydrobromic or hydrochloric acid, water, nitrogen, etc. Previously it had been assumed that, with the loss of these simple compounds and elements, intermediate products were formed which, while not necessarily stable substances, could, nevertheless, be represented structurally as having saturated valencies between all of the atoms. In such cases it was usually supposed that the exchange of groups took place at the very beginning of the process and was due to a kind of contact action produced by the particular reagent employed to induce the change. Tiffeneau came to quite a different conclusion as the result of his observations. He believes that in all intramolecular rearrangements the shifting of groups takes place not at the beginning of the operation but at a later period. Instead of intermediate products which are structurally possible and which are formed as the result of initial changes, he assumes intermediate systems which possess free valencies, and which are not, as such, capable of an independent existence, but of necessity rearrange to give structurally possible compounds.

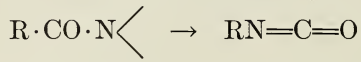
According to Tiffeneau every rearrangement takes place in two phases. There is first formed, as a result of the action of the reagent used to induce the change, a phase of *disorganization* resulting in systems of atoms possessing free valencies. In the second phase or that of *reorganization*, the atoms progressively rearrange to form stable

[1] Annalen der Chemie, **316**, 75 (1901).

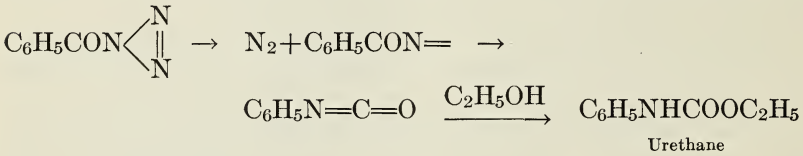
[2] Revue gen. Sci. pur. et appli. (1907), 583.

chemical compounds. Both phases probably take place simultaneously.

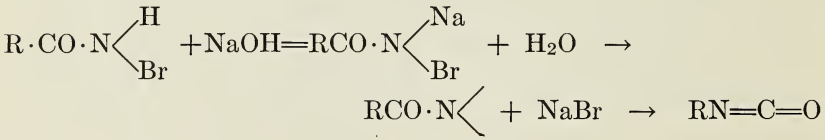
In an effort to elucidate the chemistry of intramolecular rearrangements, G. Schroeter has recently tried to consider from a common point of view those transformations which have been referred to in this text as the Hofmann, Curtius, Beckmann and benzilic acid rearrangements. Previous to this time, Stieglitz,[1] had attempted to explain the rearrangements of Hofmann and Curtius by assuming the formation of intermediate products which contain univalent nitrogen and which subsequently rearrange to give esters of isocyanic acid.



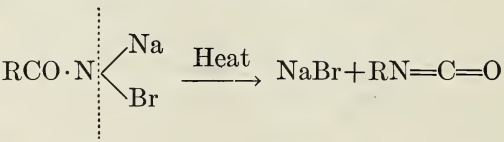
As a matter of fact, even though these intermediate esters have never been isolated, their presence has frequently been detected in the course of the Hofmann rearrangement because of their penetrating odors. They must also be formed in the course of the Curtius rearrangement:[2]



According to Stieglitz the Hofmann rearrangement, which is brought about by the action of alkaline reagents is to be interpreted as following the course indicated below:



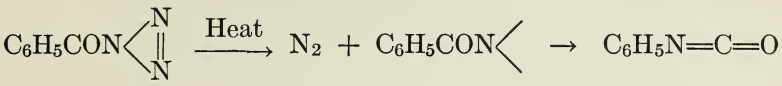
Isocyanates have been isolated as products of this rearrangement. Stieglitz[3] has shown also that the dry salts of the halogenated acid amides decompose when heated giving isocyanates:



[1] Am. Chem. Jour., **18**, 751 (1896); **29**, 49 (1903).
[2] Ber., **45**, 1058 (1912).
[3] Jour. Am. Chem. Soc., **36**, 273 (1914).

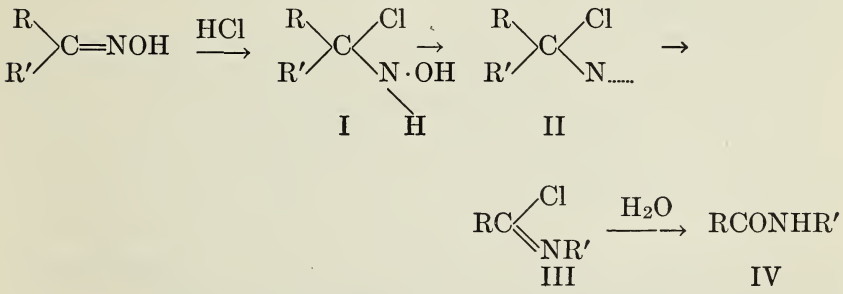
This last change is perfectly analogous to that which takes place when acylazides are heated.

Schroeter [1] has shown that the azides of organic acids are decomposed almost quantitatively when heated into free nitrogen and isocyanic acid esters:



According to Stieglitz when the formation of univalent nitrogen is interfered with, as in the case of alkyl derivatives of acid amides, no rearrangement is brought about by the reagents which favor such rearrangements in the case of non-alkylated compounds.

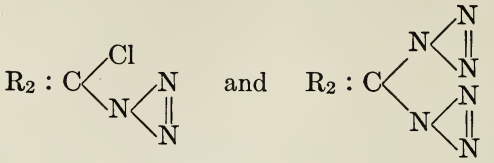
In order to apply his theory to the Beckmann rearrangement, Stieglitz was forced to postulate that hydrochloric acid is the catalytic agent which effects this change. According to his interpretation this reagent adds at the double bond giving an intermediate product corresponding to Formula I, which then loses water in the presence of the dehydrating agent (phosphorus pentachloride) and passes into the derivative, II, containing univalent nitrogen. This, being unstable, then rearranges to III, which finally interacts with water to form the anilide IV, according to the following scheme: [2]



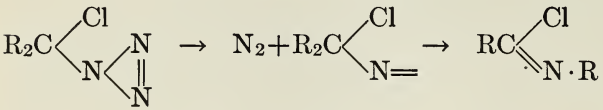
Objections to this interpretation have been brought forward by Montagne; [3] but the observations of Schroeter would seem, nevertheless, to support it. Since the intermediate products between I and IV could not, in the first instance, be isolated Schroeter tried out the reac-

[1] Ber., **42**, 2337, 3356 (1909); **44**, 1201 (1911).
[2] Stieglitz, Am. Chem. Jour., **18**, 754 (1896); **46**, 327 (1911).
[3] Ber., **43**, 2014 (1910).

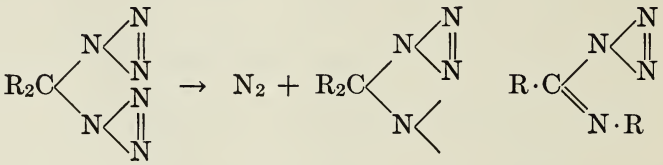
tion with compounds which possessed a certain similarity in constitution to I, i.e., with the azide-chlorides or diazides of ketones:



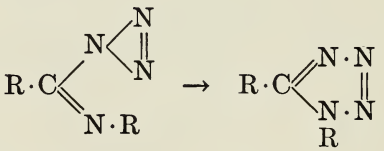
He reasoned that such compounds were capable of decomposing in a manner analogous to that which has just been given in the scheme representing the Beckmann transformation, i.e.,



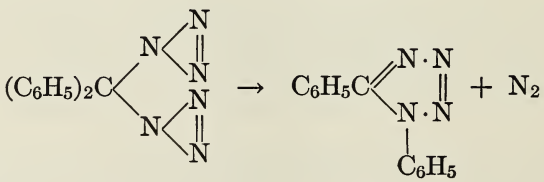
and



In the second case it was to be expected that the product would undergo the further change:



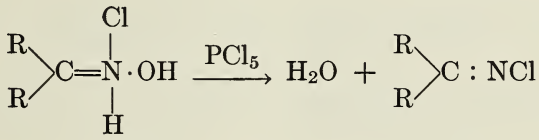
Schroeter and his co-workers actually succeeded in transforming diphenylmethane diazide (V) into N-α-diphenyltetrazol (VI)



V VI

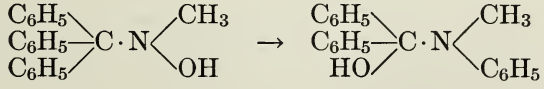
In the meantime F. Henrich and Ruppenthal [1] had discovered hydrochloric acid addition products of the oximes in the Beckmann rearrangement, and had proved that these were definitely the halogen salts of the oximes. On treatment with phosphorus pentachloride these halides pass immediately into yellow chlorides as represented in III; and which interact with water to give the acid anilides. These investigators, therefore, concluded that the formula for the intermediate product I, as given in the above scheme of Stieglitz's for the Beckmann rearrangement, must be changed to $R_2C{=}N{\cdot}OH$ ($H{\cdot}Cl$). According to Henrich and Ruppenthal, so far as present evidence goes, only those oximes which give hydrogen chloride addition products are capable of undergoing rearrangement in the presence of phosphorus pentachloride. Hydrochloric acid must, therefore, be regarded as having a definite chemical action in the Beckmann rearrangement.

A salt having the constitution assigned by Henrich would undergo dehydration giving as an intermediate product the chlorimido combination:



Halogen combinations of this type, however, do not undergo the Beckmann rearrangement according to Stieglitz and Peterson.[2] Therefore, the view that they form intermediate products seems to be untenable.

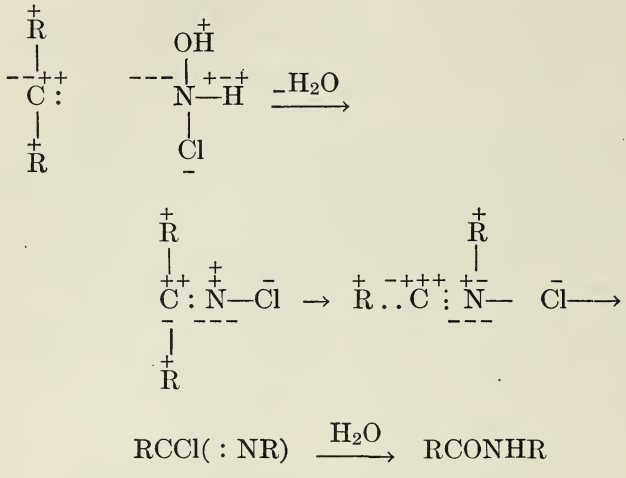
The observation by Stieglitz and Leech [3] that a rearrangement of β-triphenylmethyl-β-methylhydroxylamine is effected by the action of phosphorus pentachloride, has forced new speculations regarding the mechanism of the Beckmann rearrangement:



Here the formation of a simple univalent nitrogen derivative R_3CN is impossible. This, therefore, represents a case where the facts weigh

[1] Ber., **44**, 1533 (1911); Schroeter, Ibid., **44**, 1205 (1911).
[2] Am. Chem. Jour., **46**, 329 (1911); Ber., **43**, 782 (1910).
[3] Jour. Am. Chem. Soc., **36**, 272 (1914).

in favor of Beckmann's theory of the direct exchange of radicals.[1] The latest development in this field of speculation is the presentation of a new interpretation of the rearrangement of ketoximes based on the application of the electronic conception of organic structure. The rearrangement is expressed by this theory as follows:[2]



$$RCCl(:NR) \xrightarrow{H_2O} RCONHR$$

The conclusions of Stieglitz regarding the mechanism of these transformations are summarized in the following abstracts from one of his recent papers:[3]

(*a*) Unless conclusive evidence is brought that *salts* leading to the intermediate formation of salts of univalent nitrogen derivatives, are involved in their rearrangement, the rearrangement of β-triphenylmethyl β-methylhydroxylamine, established in this paper, the relation of stereoisomerism of oximes to their rearrangement products, established by Beckmann, Werner and Kuhara [4] would be inconsistent with the theory of the intermediate formation of univalent nitrogen derivatives in the rearrangement of hydroxylamines and at present these facts agree better with Beckmann's theory of a direct exchange of radicals or with a modification of this theory (electronic explanation). Intermediate salt formation, if established, would harmonize these facts with the univalent nitrogen theory.

[1] Ber., **27**, 300 (1894).

[2] Stieglitz and Leech, Jour. Am. Chem. Soc., **36**, 281 (1914).

[3] Stieglitz and Stagner, Jour. Am. Chem. Soc., **38**, 2064 (1916).

[4] Mem. Coll. Sci. Eng. Kyote, **1**, 254 (1903–8); **2**, 367 (1909–10); **6**, 1 (1913); **7**, 25 (1914).

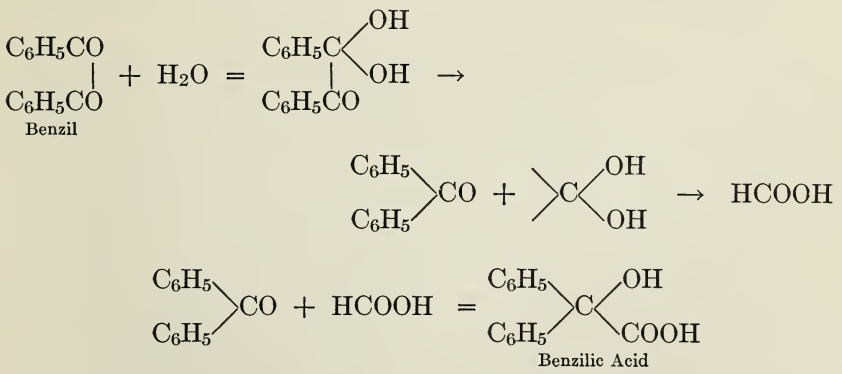
(*b*) Other facts, such as the rearrangements of azides and especially the non-rearrangement of chlorimido-benzophenones, of chlorimidoesters, and β-triphenylmethyl-β-methylchloramine, are inconsistent, without further specific assumptions, with Beckmann's theory of a direct exchange of radicals; but are in striking agreement with Stieglitz's theory of the intermediate formation of unsaturated nitrogen derivatives in the rearrangements of chloramines, hydroxylamines and azides.

(*c*) Unless further experimentation should modify these facts or their bearing, one should consider that both types of rearrangement may take place.

(*d*) Common to both theories, and the most important feature in their modern forms, is that the rearrangements originate from the tendency of unstable positive atoms Cl^+, $-O^+$, $=N^+$, etc., to go over into their stable negative forms Cl^-, $-O^-$, $N^=$, by a capture of electrons from other atoms in the same molecule, a change which is effected in the rearrangements in question. It is quite consistent with this fundamental relation that the rearrangement should go over one or the other path, the one over the unsaturated nitrogen derivatives forming probably the path of least resistance.

The most important theories advanced in explanation of the "Beckmann rearrangement" previous to 1903 have been discussed by Stieglitz in the American Chemical Journal.[1]

J. U. Nef[2] has explained the benzilic acid rearrangement by the following scheme:

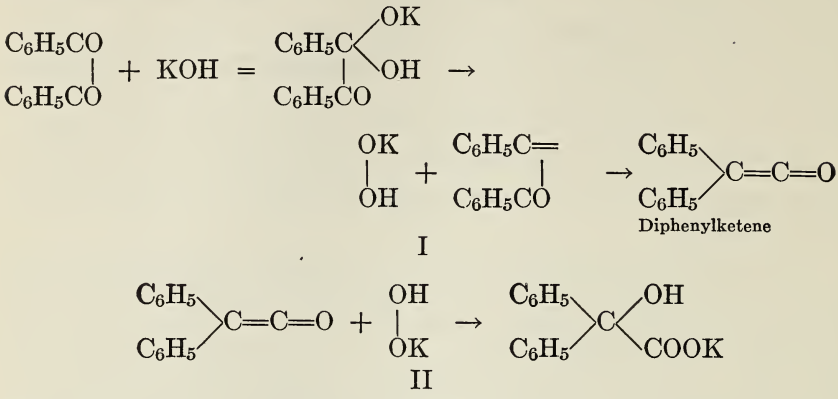


According to this interpretation benzophenone and formic acid should react to give benzilic acid, but this has not as yet been accomplished.

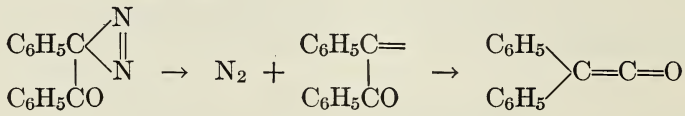
[1] Am. Chem. Jour., **29**, 49 (1903).

[2] Annalen der Chemie, **298**, 372 (1897).

G. Schroeter, therefore, modified Nef's scheme, on the basis of his experimental investigations, to the following:



While the energy involved in the reaction of diphenylketenes makes the isolation of intermediate products impossible, Schroeter and Wachendorf were, nevertheless, able to obtain diphenylketenes from benzil by starting with azo-benzil. This substance, when dissolved in an indifferent solvent and gently heated, gave a good yield of diphenylketene together with nitrogen gas.



These views of Schroeter have been tested recently by Nicolet and Pelc [1] and found to be untenable. Tiffeneau [2] recognized an analogy between the benzil rearrangement and that of pinacone into pinacoline, but Michael [3] has recently criticized severely his explanations and draws the conclusion that the benzil rearrangement is caused by "the great positive energy of the alkali employed as reagent." Lachman [4] has recently produced experimental evidence that tends to rule out the hypotheses of Nef, Tiffeneau and Michael. According to him no one of the explanations of the benzil rearrangement is capable of accounting for the actual facts. The rearrangement of dihydroxy-tartaric acid into tartronic acid [5] by the action of alkali and that of benzil into

[1] Jour. Am. Chem. Soc., **43,** 935 (1921).
[2] Rev. Gen. Sci., **18,** 584 (1907)
[3] Jour. Am. Chem. Soc., **42,** 812 (1920).
[4] Jour. Am. Chem. Soc., **44,** 330 (1922).
[5] Jour. Am. Chem. Soc., **43,** 2091 (1921).

benzilic acid are considered by him as transformations of a similar type, and he views the changes as not only rearrangements but also as intramolecular oxidation-reduction processes. He finds, for example, that benzil can be rearranged to benzilic acid by heating with water alone and that the transformation is accelerated by alkali. His interpretation of the change calls for an addition of water to each carbonyl group of benzil giving an unstable product corresponding to formula I. This, then undergoes a rearrangement with exchange of a mobile hydroxyl group for a phenyl radical giving the compound II. This, then looses water with formation of the final product of rearrangement namely, benzilic acid.

$$\underset{\text{Benzil}}{C_6H_5\cdot CO\cdot CO\cdot C_6H_5} \xrightarrow{2H_2O} \underset{\text{I}}{C_6H_5C(OH)_2\cdot C(OH)_2C_6H_5}$$

$$\rightarrow \underset{\text{II}}{(C_6H_5)_2C(OH)\cdot C(OH)_3} \rightarrow H_2O + \underset{\text{Benzilic acid}}{(C_6H_5)_2C(OH)\cdot COOH}$$

CHAPTER XX

THE BASIC PROPERTIES OF OXYGEN

In 1869 Blomstrand [1] and in 1871 Mendelejeff [2] pointed out, on the basis of purely theoretical considerations, that oxygen could react as an element possessed of more than two valencies. Four years later this assumption was confirmed experimentally by Friedel,[3] who was able to show that dimethylether combines with hydrochloric acid to give a well-defined chemical compound having the formula $(CH_3)_2O \cdot HCl$. In discussing the constitution of this body Friedel came to the conclusion that oxygen functioned as a tetravalent element. A year later Baeyer and Fischer [4] discovered addition products of fluorescein with sulphuric acid and of orcinphthalein with hydrochloric acid. In 1877 van't Hoff in his "Ansichten über die organische Chemie" pointed out the analogy between oxygen and sulphur as elements belonging to the same group in the periodic system, and indulged in speculations regarding the additive properties of oxygen. Although addition reactions are not met with so frequently in the case of oxygen as in the case of sulphur, nevertheless, four valencies appear in a great many oxygen compounds. According to van't Hoff the second pair of bonds differ in their chemical properties from the first pair. While the first two valencies are distinctly negative in character the third and fourth, although weaker, are positive and impart a basic character to oxygen. In the succeeding years still other compounds representing new combinations of acids with substances containing oxygen were discovered and the results of physico-chemical investigations demonstrated the tetravalence of oxygen.[5]

The idea of the quadrivalency of oxygen was not generally accepted, however, until about 1899. In this year Collie and Tickle [6] discovered

[1] Chemie, der Jetztzeit, 1869.

[2] Ostwald's Klassiker, No. 68, pp. 108.

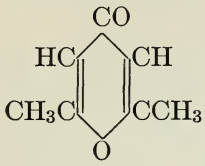
[3] Bull. soc. chimie, **24**, 166, 241 (1875).

[4] Annalen der Chemie, **183**, 1 (1876).

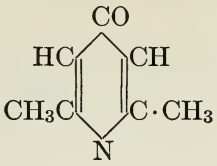
[5] Brühl, Ber., **28**, 2847, 2866 (1895); **30**, 163 (1897); **33**, 1710 (1900); Walden, Ber., **34**, 4185 (1901); **35**, 1764 (1902).

[6] Jour. Chem. Soc., **75**, 710 (1899); **85**, 971 (1904); compare Baeyer and Piccard, Annalen der Chemie, **384**, 208 (1911); **407**, 332 (1915).

that dimethyl pyrone (I) showed a very close similarity to dimethyl pyridone (II) in its behavior toward acids:



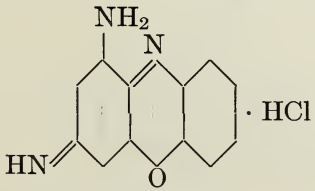
I



II

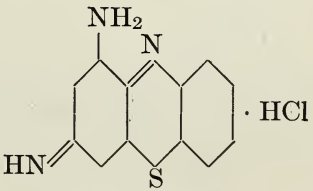
Like the latter it combines with mineral and other acids in aqueous solution to form salts as, for example, $(CH_3)_2C_5H_2O_2 \cdot HCl$. These salts combine with the chlorides of the heavy metals, etc., to form complex double salts in a manner closely analogous to the behavior of the hydrochlorides of the amines. Collie and Tickle assumed, therefore, that oxygen resembles nitrogen in possessing unsaturated residual affinities, although in a less pronounced degree. Since almost all organic compounds which contain oxygen react with acids and alkalies, it seemed quite possible that the cause for this reactivity might be found in the residual affinities of the oxygen. In order to explain salt formation in terms of this conception it was supposed that oxygen is capable of replacing nitrogen, phosphorus, and sulphur in the basic compounds of these elements. Compounds arising in this way are to be regarded as derivatives of a hypothetical base, *oxonium* hydroxide, $H_3O \cdot OH$, which belongs to the same general group as $H_4N \cdot OH$, H_4POH, H_3SOH, H_2IOH, $H_2As \cdot OH$, and whose salts can consequently be designated as *oxonium* salts. Collie's assumptions in regard to the structural formulas of dimethyl pyrone and its salts are supported by the work of Homfray on molecular refraction [1] and also by the spectroscopic measurements of Baly.[2]

In 1899 F. Kehrmann [3] arrived independently at the same conclusions as Collie and Tickle as the result of a careful study of the properties of three dyes which were at that time represented structurally by means of the following formulas:



(Oxazine derivative)

I



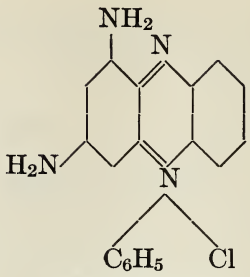
(Thiazine derivative)

II

[1] Jour. Chem. Soc., **87**, 1443 (1905).

[2] Jour. Chem. Soc., **95**, 144 (1909).

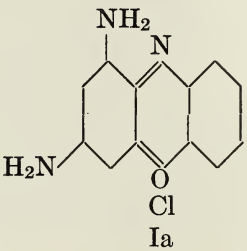
[3] Ber., **32**, 2601 (1899); Annalen der Chemie, **372**, 287 (1910).



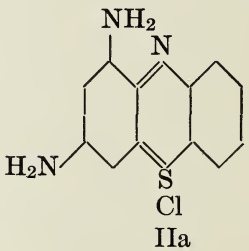
(Safranine derivative.)

III

These three combinations showed such close similarity in physical and chemical properties that Kehrmann concluded that the above formulas I and II did not represent the true constitution of the salts of the oxazine and thiazine derivatives. When after very thorough investigation it was finally established that the chloride III is to be regarded as an *ortho*quinoid azoxonium compound, Kehrmann decided that all three combinations were salts of the same order and changed the formulas of I and II to conform with this constitution, representing them as the oxonium salts Ia and IIa:

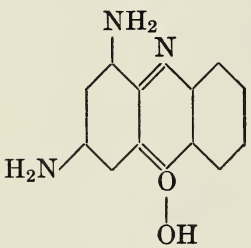


Ia

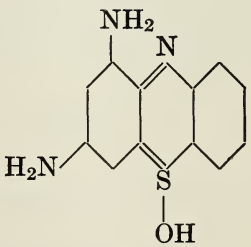


IIa

According to this conception these salts may therefore be regarded as derived from the hypothetical oxonium bases: [1]



and

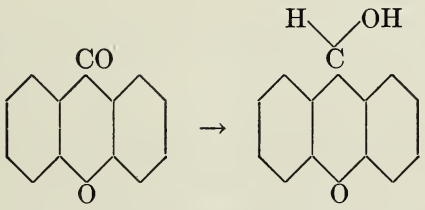


[1] Kehrmann and Lowy, Ber., **44**, 3006 (1911).

The most recent investigations of Kehrmann [1] and of Pummerer [2] seem, however, to favor a return to the original *p*-quinoid formulas.

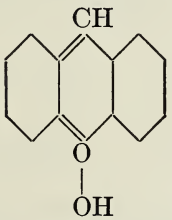
Since in addition to oxygen and sulphur, nitrogen is also present in all of the compounds investigated by Kehrmann his interpretation is open to the objection that nitrogen, rather than oxygen and sulphur, functions in salt formation and is, therefore, responsible for the basic properties of these substances.

In order to meet this objection Werner [3] undertook the investigation of cyclic oxygen compounds in which nitrogen was not present. He started with xanthone (I), a derivative of pyrone, which on reduction passes readily into the corresponding alcohol xanthydrol (II).



I II

He found that this latter compound forms salts with acids but that in so doing it does not react according to the above formula (II) but in a tautomeric manner corresponding to the isomeric formula (III).



III

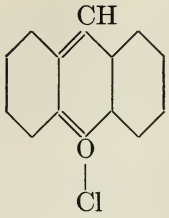
To distinguish between these two compounds Werner calls the former (II) the pseudoxanthonium base and the latter (III) the true xanthonium base. According to this conception the yellow solutions formed

[1] Ber., **47**, 1889 (1914).

[2] Ber., **46**, 2310 (1913).

[3] Ber., **24**, 3300 (1901); also "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3d Ed., p. 255, Braunschweig, 1913.

by xanthydrol and its derivatives in the presence of acids must contain oxonium salts such as, for example,



While salts of this type have not themselves been isolated they have, nevertheless, been obtained in the form of well-defined double salts with $FeCl_3$, $PtCl_4$, $HgCl_2$, etc.[1]

The interpretation of reactions in terms of tetravalent oxygen[2] became more frequent from this time on. The work of Baeyer and Villiger[3] in 1901 and 1902 was, however, the first to give the problem a really broad and general significance. They made an exhaustive study of many substances which might possibly contain quadrivalent oxygen and isolated and examined a number of salt derivatives which were formed by the action of weak acids upon ethers, alcohols, acids, esters, aldehydes and ketones. They were able to demonstrate experimentally that nitrogen and oxygen show perfect analogy in the phenomenon of salt formation since (1) oxygen salts cannot be assumed to result from the addition of acids to the double bond between oxygen and carbon, since (2) the same influences which tend to increase or decrease the basicity of nitrogen operate similarly in the case of oxygen, as for example:

H_3N (base)	H_2O (neutral)
$(C_2H_5)_3N$ (strong base)	$(C_2H_5)_2O$ (weak base), etc.

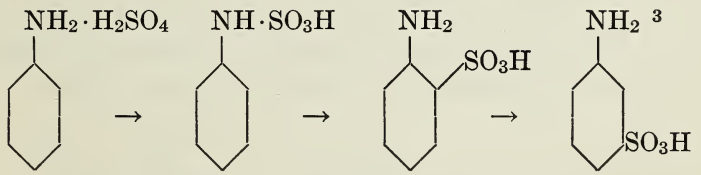
and since (3) oxygen in every form of chemical combination shows basic properties. Whether present in organic molecules in the form of an oxide—as for example in an ether—or as hydroxide or as carboxyl, oxygen always exhibits an inclination to form salts with acids and thus to bring into play its two residual valencies. It was difficult at first to find suitable acids with which to demonstrate the basicity of oxygen compounds, but Baeyer and Villiger finally discovered that

[1] Ber., **44**, 3505 (1911).
[2] Ber., **33**, 1636 (1900).
[3] Ber., **34**, 2679, 3616 (1901); **35**, 1801 (1902).

complex acids—such as ferrocyanic, ferricyanic, chloroplatinic, and even oxalic acid—could be used to advantage to prove the existence of even weak basicity.

Further impetus was given to the study of oxonium compounds through the discovery by K. A. Hofmann and his students[1] that a concentrated solution of perchloric acid will react to give oxonium salts ($\equiv O \cdot ClO_4$) which are only slightly soluble and which crystallize well. Hofmann's results seem to show that perchloric acid is superior to all other acids which have as yet been examined in this respect and is, therefore, preeminently the reagent to be used in the case of weakly basic oxonium compounds. Innumerable alcohols, ethers, aldehydes, ketones, acids and esters give salt-like derivatives which for the most part are well-defined crystalline bodies and which appear to differ in their chemical behavior in no way from the salts derived from weak bases containing nitrogen. It thus came to be generally recognized that the property which had long been regarded as characteristic of nitrogen—namely the power of passing under certain conditions from a trivalent to a pentavalent condition—was possessed also by oxygen, the only difference being that the latter element passed from a bivalent to a tetravalent condition.

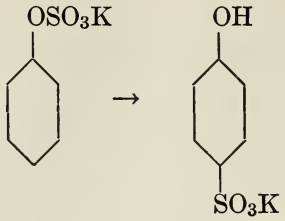
The analogy between oxygen and nitrogen is shown in yet another way. The investigations of E. Bamberger[2] have demonstrated that in the process of sulphonating aromatic amines, and in particular aniline, the amino group is attacked first. The sulphate which is formed in this way readily splits off water, passing into a sulphamine combination which finally undergoes molecular rearrangement giving *ortho*- and *para*-sulphanilic acids:



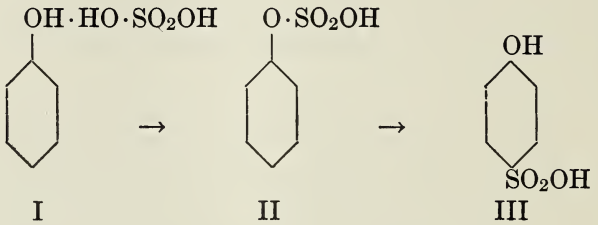
Baumann[4] observed a perfectly analogous reaction for phenols as early as 1878 when he discovered that potassium phenyl-sulphate

[1] Ber., **43**, 178, 183, 1080, 2630 (1910); **42**, 4856 (1909).
[2] Ber., **30**, 654, 2274 (1897).
[3] H. Wieland, Ber., **40**, 4269 (1907).
[4] Ber., **11**, 1909 (1878); Schmitt, Jour. prakt. Chemie, **31**, 409 (1885); Claisen, Ber., **33**, 3780 (1900), etc.

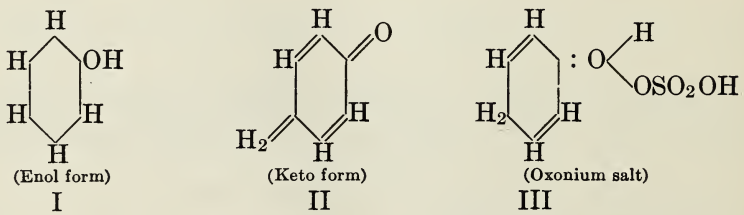
rearranges upon heating to give the potassium salt of phenol-*p*-sulphonic acid:



In the process of sulphonating phenol it may be assumed that salt formation represents an intermediate stage in the reaction and that it results in the formation of an unstable addition product (I). Under the conditions of the reaction this then loses water to give the phenyl ester (II) and this in turn isomerizes to form the sulphonic acid derivative (III).



Kendall, who has recently investigated the ability of sulphuric acid to add to phenol combinations,[1] postulates that the sulphonation of a phenol is preceded by the formation of an addition product of the nature of an oxonium salt. Whether this involves a tautomeric change of phenol I into its ketonic modification II [2] followed by addition on the oxygen III as in the case of alcohols [3] is not as yet known.

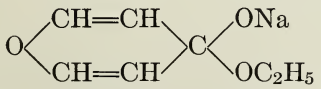


[1] Jour. Am. Chem. Soc., **36**, 2507 (1914).
[2] Gomberg and Cone, Annalen der Chemie, **376**, 220 (1910),
[3] Maass and McIntosh, Jour. Am. Chem. Soc., **34**, 1284 (1912).

The objection has been raised that these so-called oxonium salts are really molecular compounds and that they are, therefore, analogous in structure to such substances as, for example, are formed by the reaction of the picrates with aromatic hydrocarbons. This objection has, however, been met by Walden [1] who has demonstrated by means of physico-chemical measurements that the compounds formed by the union of dimethyl pyrone with acids are actually true salts, and that solutions of such salts have the properties that are to be expected in salt combinations arising from the union of a weak base and a relatively strong acid. Walden's experiments included the determination of (1) mutarotation of grape sugar in the presence of dimethyl pyrone due to the formation of hydroxyl ions, (2) the coefficient of distribution of picric acid between water and benzene as compared with that of picric acid plus dimethylpyrone, (3) the lowering of the freezing point of pure hydrochloric acid in aqueous solution as compared with that of hydrochloric acid solution plus dimethyl pyrone, and (4) the conductivity of dimethyl pyrone alone as compared with that of dimethyl pyrone plus an acid (picric acid) determined in different solvents such as (*a*) liquid sulphur dioxide, (*b*) acetonitrile and (*c*) water.

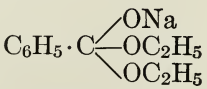
Walden found as a result of these experiments that dimethyl pyrone is a weak base slightly stronger than urea but much weaker than aniline. At the same time he was able to show that under certain conditions it may be slightly acidic in character. The substance may be regarded, therefore, as an amphoteric body showing a tendency to form hydrogen as well as hydroxyl ions in solution.

In connection with the acid properties of pyrone derivatives it is to be noted that Willstätter and Pummerer [2] made the independent observation that pyrone itself possesses the properties of a weak acid and has the ability to add sodium and potassium alcoholates in alcohol solutions. They regard the change as perfectly analogous to that which Claisen [3] concludes takes place when esters of organic acids interact with alcoholates, and which he represents as addition to the unsaturated C=O group with formation of carbonium compounds:



(Pyrone addition-product)

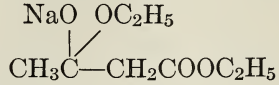
and



(Ethyl benzoate addition-product)

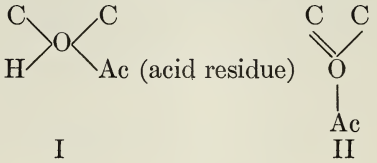
[1] Ber., **34**, 4189 (1901); **35**, 1764 (1902); Sackur, Ber., **35**, 1242 (1902).
[2] Ber., **37**, 3740 (1904).
[3] Ber., **20**, 646 (1887).

Willstätter differs, however, from Claisen in his interpretation of the mechanism of the reaction and assumes that sodium ethylate adds to the oxygen of ethyl acetoacetate to give



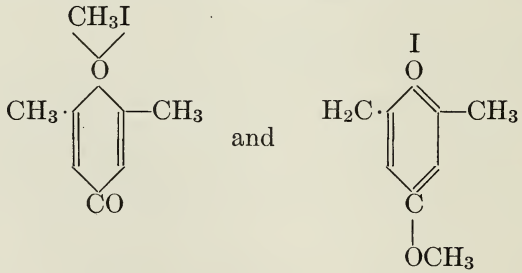
as an intermediate product of the reaction.

Oxygen has thus been shown to possess basic properties and it is now assumed by many chemists that its salts with acids are of the type of ammonium salts. Combinations in which oxygen functions as a tetravalent element are called oxonium compounds,[1] and may be formulated in such a way as either to correspond to the salts of the tertiary nitrogen bases as in (I), or to the quaternary nitrogen bases as in (II).



I II

The possibility of two types corresponding to the above formulas was first recognized when Kehrmann [2] discovered a well-defined addition product of methyl iodide with dimethyl pyrone. While a number of different structural formulas are posssible in the case of this substance only two were seriously considered by Kehrmann, viz.:



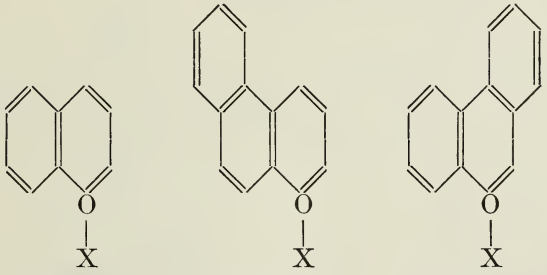
and of these the first seemed to him to be the most probable. Baeyer [3] was, however, able to show later that the second formula expresses the chemical properties of the substance better than the first and that it must, therefore, be regarded as a substitution-product of a cyclic combination to which Baeyer assigned the name *pyroxonium iodide*, or in other words as dimethyl-methoxy-pyroxonium iodide

[1] E. Wedekind, Ber., **38**, 421 (1905).

[2] Ber., **39**, 1299 (1906).

[3] Ber., **43**, 2337 (1910); Hofmann, ibid., **43**, 2630 (1910).

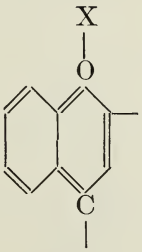
Soon after Werner's discovery of the xanthonium bases, the salts of the phenylated xanthonium compounds and of the substituted phenyl derivatives were investigated by H. Decker and Bünzly [1] and by Kehrmann [2] respectively. This work was followed by the discovery of colored pyryllium salts by Decker and von Fellenberg.[3] The latter obtained a number of typical compounds which could not be regarded either as acid addition products or as derivatives of basic carbon. These substances correspond to the following formulas in which X represents the acid radical and which must be assumed to contain tetravalent oxygen:



Salt of benzopyryllium [4] | Salt of naphthopyryllium | Salt of diphenylpyryllium

As a result of these investigations Decker concludes that " tetravalent basic oxygen must in the future take its place beside pentavalent nitrogen, tetravalent sulphur, and trivalent iodine and must be regarded as functioning in much the same way as these elements in ring structures."

According to Willstätter [5] the colored anthocyanins and their hydrolytic products the anthocyanidins must be regarded as *o*-quinoid oxonium compounds and, therefore, belong to the class of benzopyryllium derivatives:



[1] Ber., 37, 2931 (1904).

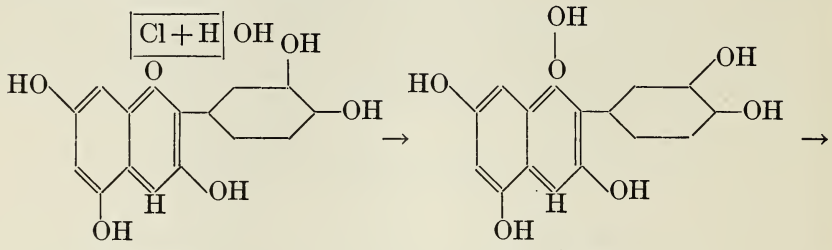
[2] Ber., **41**, 3440 (1908); 42, 870 (1909); **44**, 3505 (1911); **47**, 3052 (1914); also compare von Braun, Ber., **49**, 191 (1916).

[3] Annalen der Chemie, **356**, 281 (1907); **364**, 1 (1909).

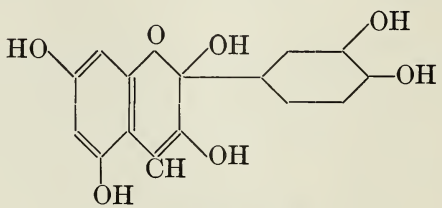
[4] Jour. Prakt. Chemie, **94**, 54 (1916).

[5] Annalen der Chemie, **401**, 189 (1913); **408**, 1 (1915); **412**, 113 (1916).

These substances occur in the coloring matter of plants and have been made the subject of an exhaustive investigation by Willstätter and his students. They all possess the characteristic property of losing color gradually in aqueous and alcoholic solutions and of regaining it again upon the addition of acid. Earlier investigators who observed this change in color interpreted it as due to the reduction of the coloring matter, but Willstätter has been able to show that the reaction is somewhat more complicated. He explains it by supposing that the salt is first hydrolyzed to an oxonium- or color-base and that this then isomerizes to give a pseudobase or carbinol:

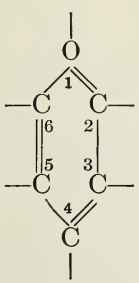


Colored salt — Violet colorbase



Colorless pseudo base

Von Baeyer[1] subsequently prepared a series of simple derivatives of pyryllium

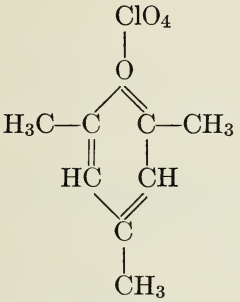


in which methyl, methoxy, phenyl and other groups replace the hydrogen of the ring. This work was carried out in co-operation with J.

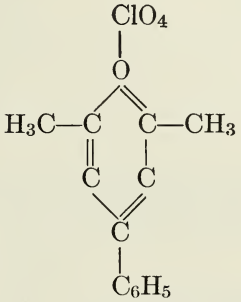
[1] Ber., **43**, 2337 (1910).

Piccard [1] and others and demonstrated beyond a doubt that oxygen possesses decidedly basic properties and is able to form well-defined salts.

In comparing the perchlorates of alkyl and aryl derivatives of pyryllium it was observed that the former are colorless while the later are colored compounds. For example 2, 4, 6-trimethylpyryllium perchlorate (I) is colorless, while 2, 6-dimethyl-4-phenylpyryllium perchlorate (II) is as yellow as sulphur.

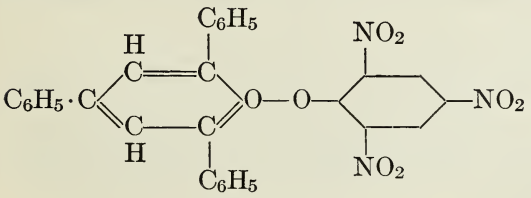


2-4-6-Trimethylpyryllium perchlorate

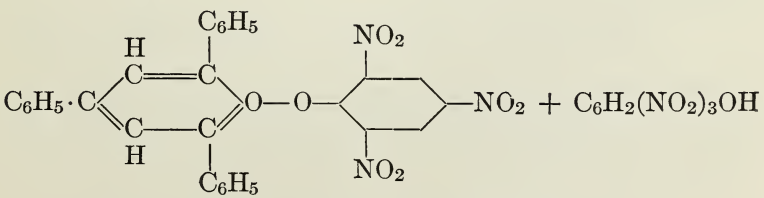


2-6-Dimethyl-4-phenyl-pyryllium perchlorate

Triphenyl-, phenylanisyl-, and trianisyl-pyryllium have been prepared by W. Dilthey [2] and have been found to possess greater basicity than the corresponding trimethyl derivative. This is illustrated by the fact that the acetate of trianisylpyryllium is stable in aqueous solution. These salts are all brightly colored and exhibit the phenomenon of halochromism. For example, the triphenyl derivative of pyryllium reacts with picric acid to give a red monopicrate and a yellow dipicrate:



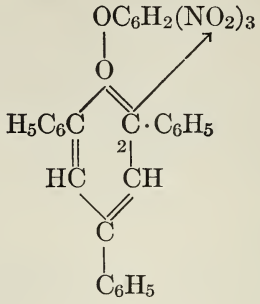
and



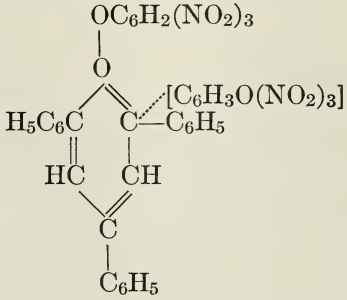
[1] Annalen der Chemie, **384**, 208 (1911); **407**, 332 (1915).

[2] Jour. prakt. Chemie, **94**, 53 (1916); **95**, 107 (1917).

Interpreted in the sense of Pfeiffer's theory this phenomenon may be explained by supposing that the addition of the first molecule of acid acts to increase greatly the unsaturation of the carbon atom in position 2.



This would account for the red color of the salt and also for its ability to add a second molecule of acid in this position:



The formula of the dipicrate indicates that it is more highly saturated than the monopicrate and that a *priori* it might, therefore, be expected to show a weaker coloration.

It is evident [1] that the conception of tetravalent oxygen affords a satisfactory and an exact interpretation of many reactions and it frequently happens that such explanations are more plausible than those which they have superseded. Ester formation, for example, is usually expressed in the following way:

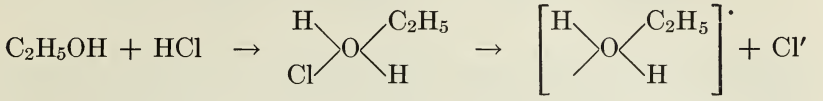
$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$

But this offers no explanation as to why the rate of esterification is so greatly accelerated by the presence of acids or, in other words, by the presence of hydrogen ions. H. Goldschmidt [2] has recently shown, as a result of his researches on the rate of esterification, that the reaction

[1] H. Kauffmann, "Die Valenzlehre," p. 185.

[2] Zeitschr. Elektrochemie, **14**, 581 (1908)

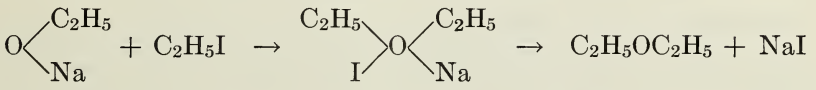
consists primarily in the addition of a hydrogen ion to a molecule of alcohol with the formation of the complex ion ($C_2H_5OH_2$). In terms of the quadrivalence of oxygen it may be assumed that the formation of the complex positive ion takes place as the result of the addition of the acid, as, for example HCl, to the alcohol, followed by the immediate dissociation of the products. Thus:



The positive ion which is formed in this way then reacts with a molecule of acid in the following manner:

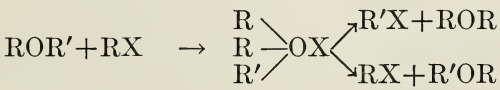
$$C_2H_5OH_2 \cdot + CH_3COO' \rightarrow CH_3COOC_2H_5 + H_2O$$

The formation of ether by the interaction of ethyl iodide and sodium alcoholate may be regarded as an analogous transformation:



For other examples, the reader is referred to the original papers mentioned in this chapter and also to the work of E. Fromm.[1]

A study of the mechanism of the Grignard reaction has given further confirmation of the hypothesis of oxonium salt formation. Combinations which contain quadrivalent oxygen are apparently formed as intermediate products in the application of this reaction in ether solution and evidence of heterosposis has been obtained. For example an oxonium salt of this type can decompose in either of two ways:[2]



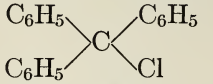
The American investigator Gomberg is very strongly opposed to the prevailing ideas in regard to the tetravalency of oxygen in organic combinations containing this element. He does not believe that the arguments in favor of the *oxonium* constitution of dimethyl pyrone salts and related compounds are sound, and has put forward the view that the compounds generally considered as oxonium salts should be regarded as *carbonium* compounds.[3] Gomberg advocates a quinonoid

[1] Annalen der Chemie, **396**, 75 (1913).

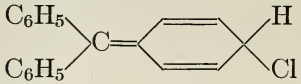
[2] Stadnikoff, Ber., **44**, 1157 (1911); Tschelinzeff, Ber., **37**, 4534 (1904).

[3] Gomberg and Cone, Annalen der Chemie, **370**, 142 (1909); **376**, 183 (1910).

constitution for the colored salts of triphenyl carbinol and related compounds, and explains the unique behavior of such salts by supposing that they are capable of existing in two isomeric modifications the one aromatic and colorless (I), and the other quinonoid and colored (II).

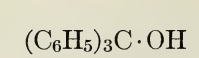


I

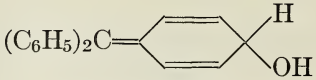


II

Gomberg is of the opinion that a large number of the organic derivatives which contain oxygen possess a quinocarbonium configuration and he considers it unnecessary to assume an oxonium structure for these combinations. He has furthermore shown that a number of the carbinols are capable of existing in both the quinoid and benzoid state.[1]

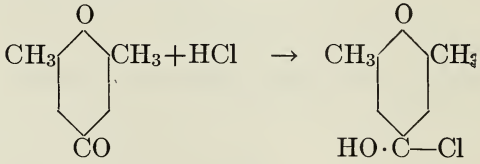


Carbinol (pseudo-base)

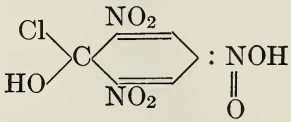


Quinocarbonium base

Gomberg and his collaborators have not only made a number of applications of their quinocarbonium hypothesis, but they have also succeeded in bringing the salts of dimethyl pyrone into line with those which have just been considered. Gomberg and Cone [2] emphatically deny the formation of an oxonium salt when dimethyl pyrone combines with an acid, and interpret the reaction as taking place by addition according to the scheme:

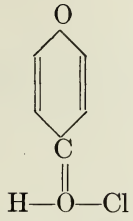


In other words, the reaction depends upon the presence of the carbonyl group, and addition results in a carbonium salt. The behavior of picric acid towards hydrochloric acid has been explained in a similar way by Stepanoff [3] who assumes the formation of the following carbonium salt:



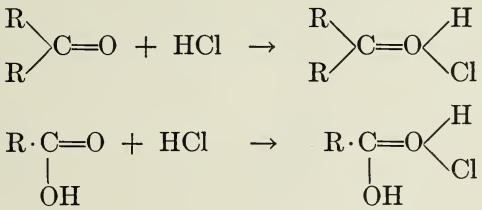
[1] Jour. Am. Chem. Soc., **35**, 1035 (1913).
[2] Annalen der Chemie, **376**, 217 (1910).
[3] Annalen der Chemie, **373**, 219 (1910).

The principal opposition to the extension of the class of carbonium salts by Gomberg has come from Kehrmann,[1] although recently Kendall has also given support to the oxonium theory.[2] The latter has investigated the action of organic acids on dimethyl pyrone and considers that these addition products are true oxonium compounds and that they are to be expressed structurally as follows:

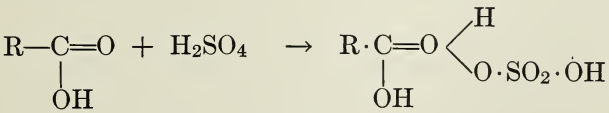


Hydrochloride of dimethyl pyrone

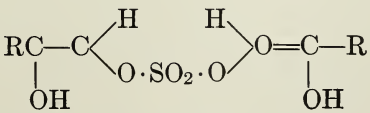
He considers that their formation is due to the basic properties of the unsaturated C=O group and that oxygen functions as a quadrivalent element. Kendall[3] disagrees with Gomberg and Cone and concludes from the results obtained in his experiments that organic acids, aldehydes and ketones all interact with acids in an analogous manner giving oxonium compounds:



He also concludes that the compounds formed by the addition of sulphuric acid to organic acids are true oxonium salts and represents them structurally as follows:



and



[1] Annalen der Chemie, **372**, 287 (1910).
[2] Jour. Am. Chem. Soc., **36**, 1242 (1914).
[3] Jour. Am. Chem. Soc., **36**, 1722 (1914); **37**, 160 (1915).

Ismailskii,[1] who has made a critical examination of the proposed hypotheses in connection with the relation between color and structure, considers that both the carbonium and the quinone-carbonium hypotheses are inadequate to account for the various phenomena of halochromism. For other speculations dealing with the question of basic properties of oxygen the reader is referred to publications by McIntosh[2] and Dehn.[3]

[1] Jour. Russ. Chem. Soc., **47**, 63 (1915); Chem. Abstr., **9**, 1471 (1915).

[2] Jour. Chem. Soc., **85**, 919, 1098 (1904); Jour. Am. Chem. Soc., **27**, 26, 1013 (1905), **28**, 588 (1906); **30**, 1097 (1908); **32**, 542 (1910); **33**, 71 (1911); **34**, 1273 (1912).

[3] Jour. Am. Chem. Soc., **39**, 2646 (1917).

CHAPTER XXI

THE THEORETICAL SPECULATIONS OF ARTHUR MICHAEL

As early as 1878 van't Hoff had pointed out in his "Ansichten über die organische Chemie" [1] that many organic reactions, which were at that time regarded as processes of substitution, could be considered as transformations involving addition reactions. Arthur Michael arrived at the same conclusion as the result of systematic experimental research. His investigations led him to conclude that, in general, addition reactions play a much more important part in chemical processes than had previously been assumed, and that they frequently serve as preliminary or intermediate stages in other types of transformations. Kekulé more than fifty years earlier had given definite expression to the conception of molecular-addition as forming an intermediate process in chemical change. This is diagramed below, although it has already been referred to in a previous chapter in this book.

Before chemical action | Addition product | After chemical action

Intermediate products, corresponding to expression 2 in the diagram, must undoubtedly have been obtained frequently in the course of investigations in the past, but for many years it was impossible to establish their existence in a sufficient number of cases to meet all objections, and only in recent times have investigators produced enough experimental evidence to establish their very general occurrence. The study of chemical phenomena gradually forced chemists to the assumption of intermediate mobile combinations in organic reactions, and in 1907 Emil Fischer gave expression to a feeling universally prevalent at that time in the following words: "the conviction is gaining ground more and more that, very generally and even in the ordinary processes of substitution, transitional addition reactions take place in the sense

[1] Vol. I, 225, 244.

that Kekulé and others have regarded as probable."[1] Emil Fischer has since greatly extended this conception as has already been noted in a previous chapter of this book. Even in catalysis there is the assumption that an intermediate product, consisting of catalyst and substrata, is formed since this in most cases offers the best explanation of the facts.[2] Recently methods have been devised by which the existence of such intermediate products can be demonstrated. In addition to the optical methods which have already been referred to, the so-called thermal analysis[3] may be mentioned. This has been made practical for organic chemists through the work of R. Kremann,[4] Ph. Guye and his students, Holleman[5] and J. Schmidlin.[6]

A. Michael, convinced of the general applicability of Kekulé's conception, endeavored to determine what forces induced and regulated this type of chemical reaction, and he came to the conclusion that changes in energy were the important controlling factors; for it was to be noted that problems dealing with chemical affinities found their best solution within the sphere of energy relations. The experiments by means of which he endeavored to trace valence and the course of chemical processes back to the energy relationships of the atoms, have been published in a series of articles.[7] An outline of what is fundamental in Michael's system is all that can be given here, but it is hoped that this may serve as an introduction to a more thorough study of his work. The author's own words will be quoted frequently in an effort to avoid any misunderstanding of his conceptions and deductions since these are often extremely subtle.

Every atom represents a definite quantity of potential chemical energy. Every unsaturated (free) atom has a more or less definite tendency toward a condition of greater stability and if it finds no other atoms of a different element with which to combine, it will combine eventually with one or more atoms of its own kind. When chlorine atoms, for example, unite to form a molecule, their free atomic energy

[1] Ber., **40**, 495 (1907); Walden, Ber., **32**, 1850 (1899).

[2] Bredig, Ber., **41**, 754 (1908).

[3] S. R. Kremann, "Über die Anwendung der thermischen Analyse zum Nachweis chemischer Verbindungen," Bd. **14**, der Sammlung chem. u. tech-chem. Vorträge, p. 213 (1909).

[4] Monatsh. Chemie, **25**, 1215 (1904); **27**, 125 (1906); **28** (1907).

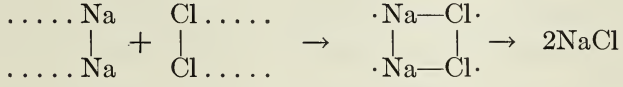
[5] " Die direkte Einführung von Substituenten in den Benzolkern," p. 26, Leipzig, 1910.

[6] Schmidlin and Lang, Ber., **43**, 2806 (1910); **45**, 899 (1912).

[7] Jour. prakt. Chem., **37**, 523 (1888); **40**, 178 (1889); **60**, 286, 409 (1899); **68**, 487 (1903); **75**, 105 (1907); Ber., **33**, **34**, **36**, **38**, **39**, 203, 2138, 2143, 2149, 2157, 2569 (1906); "Stereoisomerism and the Law of Entropy," Am. Chem. Jour., **39**, 1 (1908).

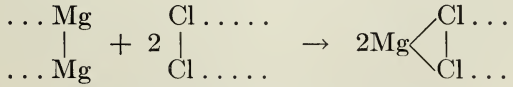
is partly used up as heat, partly changed into bound energy, and partly persists as free energy within the molecule. Bromine atoms and bromine molecules show analogous, though relatively smaller amounts of free energy, as do similarly all atoms and all molecules whether made up of atoms of the same kind or of different kinds. The tendency of atoms to combine with each other Michael calls polymerization, and he represents it as a periodic function of the atomic weight. This very interesting development can only be alluded to in this brief review.[1]

When sodium reacts with chlorine the process in terms of the Kekulé-Michael conception is to be conceived as follows: "when a molecule of sodium comes within the sphere of attraction of a molecule of chlorine, the two molecules are drawn together by the action of their free energies and merge to form a double molecule. Since, however, sodium and chlorine mutually attract each other, the bound energy between atoms of the same kind no longer suffices to hold these atoms together, with the result that the double molecules suffer a rearrangement and finally a decomposition into two molecules of sodium chloride. If the free energy be represented by dotted and the bound energy by solid lines, this process may be depicted by means of the following diagram:



As a result of this change the free energy of the sodium and the chlorine is changed into bound energy and heat and simultaneously the bound energy between atoms of the same kind disappears, being converted in part into bound energy between atoms of sodium and chlorine (unlike atoms) and in part into heat.

In other changes, dependent upon the nature of the elements involved, the interchange of the energy relations is not so complete. When, for example, a chlorine molecule reacts with a magnesium molecule, the bond between the two magnesium atoms is broken, while on the other hand, the energy of the relatively weaker magnesium atoms is not sufficient to completely sever the bond between the two chlorine atoms. According to Michael a new molecule is formed containing only a part of the original bound energy uniting the two chlorine atoms, and in which there is decidedly more free energy for each chlorine atom than is to be found in the molecule of sodium chloride. Thus:



[1] Jour. prakt. Chemie, **60**, 293 (1899).

On the other hand, atoms of magnesium and oxygen may be regarded as almost completely neutralizing each other and this accounts for the fact that magnesium oxide is such an indifferent chemical compound. Again, oxygen does not fully neutralize the bound energy of the alkali metals and thus oxides arise in which the metallic atoms are combined not only with oxygen, but are also in direct union with each other.

While it has been assumed previously that valency was the measure of the total affinity of the atoms, in terms of Michael's conception, valency becomes merely a rough measure of the resultant of the chemical attractions, operating directly or indirectly between atoms.[1] This conception supposes that the processes in operation during an exchange of atoms are analogous to the processes at work during neutralization as in the case of acids and bases. The well-known phrase—" every system tends to a condition representing the maximum of entropy "—may be correctly applied in determining the course of organic processes if the term " chemical neutralization " is substituted for the term " entropy." This phrase may be applied most advantageously to reactions involving unsaturated atoms, since in such cases it is often possible to predict which will be the more favorable of all conceivable neutralization phases. This so-called neutralization principle may be briefly formulated in the following words: " *Every chemical system tends to so arrange itself that the maximum of chemical neutralization is attained.*" [2]

Michael regards the atoms themselves as the fundamental units involved in any process of chemical neutralization, and makes a sharp distinction between positive and negative units. According to him the more strongly negative elements are the halogens, especially chlorine, while elements like oxygen and nitrogen are more weakly negative. Potassium and sodium are to be regarded as strongly positive while magnesium and silver are weakly positive, and mercury is very weakly positive. Furthermore, he believes that every chemical compound, even if from its valence formula it appears to be saturated, contains more or less free chemical energy. This follows from the fact that the free energies of its component atoms never completely neutralize each other during combination. The free chemical energy, considered together with the affinity relationships of the atoms involved, determines the chemical potential of any system. The meaning of this conception is expressed in the following sentences: "a sufficient chemical potential is necessary in order that a given reaction may take place. This is dependent upon two factors: first, free chemical energy and second,

[1] Jour. prakt. Chemie, **68**, 489 (1903).
[2] Jour. prakt. Chemie, **60**, 292, 300 (1899).

the affinity relations between the reacting atoms; neither factor alone is capable of inducing a reaction.[1]"

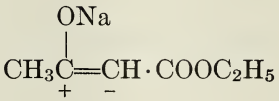
The properties of the element carbon are in complete harmony with its position in the periodic system. This has already been pointed out by van't Hoff,[2] who has emphasized the fact that carbon occupies a transitional position between the most widely different pairs of elements and that to its double nature is due its ability to enter into combination with so many other elements. Since, moreover, the chemical behavior of an element depends upon the nature of the atoms which are in union with it, it follows that carbon, since it is itself relatively neutral in character, must be exceptionally susceptible to outside influences and that its chemical properties should therefore vary in the directions determined by such influences. Each and every element may thus impart its properties to a greater or less degree to the element carbon. This extremely important property of carbon—the realization of which is fundamental to an understanding of organic chemistry—has been called by Michael its "chemical plasticity"[3] Hydrogen is the only other element which compares with carbon in the degree to which it possesses this property. The fact that carbon is essentially a weakly negative element and that the positive-negative difference between carbon and hydrogen is slight, serves to explain why even minor changes in the constitution of organic compounds materially influence the properties of these atoms.[4]

Michael also developed special conceptions in regard to the condition of unsaturation. The fact that free methyl does not exist tends to show that the presence of three hydrogen atoms bound to carbon does not interfere with the ability of the carbon atom to undergo polymerization. When a methyl group unites with a second like group the two carbon atoms, which were previously unsaturated, enter into chemical combination and simultaneously a change in the chemical properties of the hydrogen and of the carbon atoms takes place. Again, "if one hydrogen atom is removed from each of the carbon atoms of ethane the energy, which was previously exerted in holding these hydrogen atoms, may be used in part to strengthen the mutual saturation of the carbon atoms or in part in changing the relative relation existing between these carbon atoms and their respective remaining hydrogen atoms." The increased self-saturation of the carbon atoms in such compounds offers a sufficient explanation for the fact that the

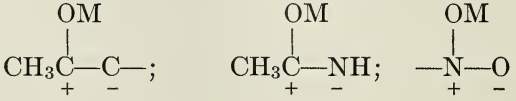
[1] Annalen der Chemie, **363**, 21 (1908).
[2] "Ansichten über die organische Chemie," I, 280; II, 242 (1878–1881).
[3] Jour. prakt. Chemie, **60**, 325 (1899).
[4] Jour. prakt. Chemie, **37**, 522 (1888).

unsaturated carbon atoms of the ethylene series show no tendency toward polymerization. "It is obvious that if several carbon atoms in a molecule are simultaneously unsaturated, relations of multiple self-saturation between the adjoining or directly bound atoms must result, and that, further, if the number of such unsaturated atoms is uneven, the odd atoms of two molecules must enter into a simple chemical combination with each other, except in such special cases as when this carbon atom is subject to strongly negative influences. According to this conception of unsaturation a two-membered system of such atoms represents not merely a store-house of potential chemical energy, but also a relatively increased self saturation of its unsaturated atoms." [1]

Just as the elements of inorganic chemistry are able to combine with one another in a great variety of ways, it happens that organic compounds are frequently formed which contain atomic groupings endowed with pronounced positive or negative properties as, for example, ethyl acetoacetate, which combines with sodium to form a sodium derivative:



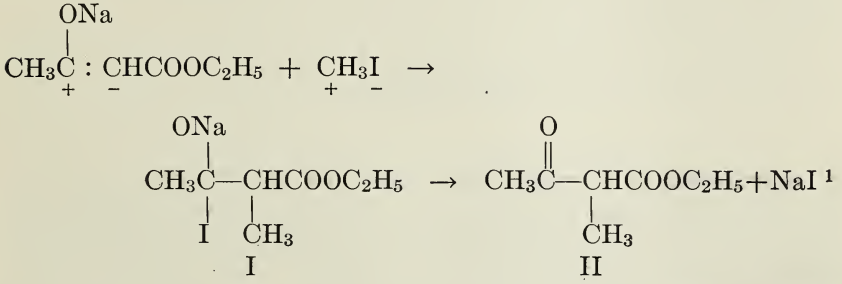
Other examples of this type may in general be found in compounds with the atomic groupings



When the metallic derivative of such a substance interacts with an alkyl halide, as, for example, methyl iodide, several atomic forces are involved in bringing about a separation of the iodine from the methyl group. According to Michael, the dissociation of the halide will depend principally upon the attraction of the metal for iodine as compared with the relative attraction of the metal for oxygen, and of one of the unsaturated atoms in the molecule for methyl. The more positive the metal, the more readily will the methyl tend to combine with that one of the unsaturated atoms which is most negative in character. This is due to the fact that the attraction of oxygen for methyl is less than that of the unsaturated carbon atoms, since the former is directly bound to the strongly positive metal while the latter are more remote from this influence. In other words the positive character of the metal

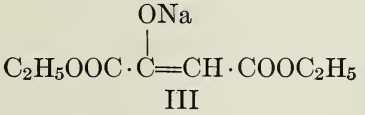
[1] Jour. prakt. Chemie, **60**, 298 (1899).

usually operates in such a manner as to direct the course of the reaction. It may happen, however, that the properties of the unsaturated atoms have been so changed by substitutions in the molecule, as to make their attraction for methyl less than that of oxygen, in which case the course of the reaction will be altered and methyl will combine directly with oxygen. In the case of ethyl acetoacetate and methyl iodide the reaction may be considered as proceeding by addition with the formation of a carbon homologue. Thus ethyl methylacetoacetate will be the product of the reaction and may be regarded as resulting from the decomposition of the addition product (I) into sodium iodide and the β-ketone ester (II):



It is also possible that the attraction of sodium for iodine and of methyl for the negative unsaturated carbon atom may in themselves be sufficiently powerful to bring about a direct reaction without the formation of an intermediate addition product.

If, however, the more negative carbethoxy radical replaces the methyl group of ethyl acetoacetate, as for example in

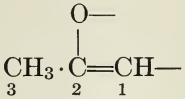


the course of the reaction with methyl iodide is changed and the production of carbon homologues becomes so difficult that at best only poor yields of these substances are obtained. Under these conditions oxygen substitution products are formed and this may be explained as resulting from the relatively increased attraction of the oxygen for methyl, which in turn is due to the influence of the neighboring carbethoxy group. At the same time the tendency of the unsaturated methine

[1] Michael believed at one time that he had succeeded in isolating such an addition product [see Ber., **38**, 3220 (1905)] corresponding to formula I, but this was contested by C. Paal [see Ber., **39**, 1436 (1906)].

grouping to undergo polymerization is depressed. Moreover, since the tendency toward carbon homology is slight in the case of such compounds the formation of oxygen-homologues ought to be still further favored by the substitution of weakly positive silver in place of the strongly positive sodium or potassium. As a matter of fact it has been shown that esters of methoxy-fumaric acid may be obtained in this way.

If the conception of the plasticity of carbon be applied to the interpretation of the ethyl acetoacetate synthesis the difference observed in the reactions of the substances just cited is still more readily explicable. In the sodium salt of ethyl acetoacetate the oxygen bound to the metal, and the carbon of the methine group occupy the same relative position in the molecule with respect to the methyl group



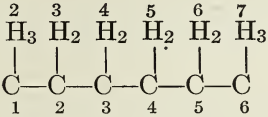
By substitution of a negative carbethoxy for methyl not only is the character of the whole molecule changed, but the influence of this group upon the carbon of the methine radical is greater than upon the oxygen because of the plasticity of the former element. The result is that in the reaction with methyl iodide the possibility of addition of methyl to carbon is decreased. Thus Michael introduced new conceptions based upon the principle of neutralization in place of the old idea of double decomposition and formulated the following general rule: In any reaction the most favorable neutralization is realized when combination takes place between those atoms or radicals which are endowed with pronounced chemical properties. In cases where the reacting bodies possess neither unsaturated atoms nor systems of atoms with so-called double bonds, thus offering simultaneously the possibility of mutual saturation, combination takes place between the remaining residues. In any case the further course of the reaction depends upon the relative attractions of the atoms which take part in the change.[1]

van't Hoff has already pointed out [2] that, in considering the total attraction which two atoms in a molecule exercise toward each other, it is necessary to consider not only the nature of the atoms (i.e., their relative positive or negative character), but also their spacial relations in the molecule. It is possible in this way to subdivide the total attraction of the atoms into forces which operate directly in space and forces which operate indirectly through chemical combination or through

[1] Jour. prakt. Chemie, **60**, 324 (1899).

[2] "Ansichten über die organische Chemie," 1, 284; Vol. 2, 252.

other atoms. On the basis of this conception Michael has worked out a scheme showing the relative sequences of the space relationships for normal paraffines.[1] In conformity with the nomenclature agreed upon at Geneva a chain of atoms may be provided with numerals in such a way that starting with a given carbon atom, not only the succeeding carbon atoms but also the other atoms in the system are numbered. For example:



According to our present knowledge, then, the sum of all the attractions which a given atom exercises for every other atom in the molecule may be represented by the following scheme showing the relative scale of the positions of the atoms:

1—2—3—5—6—4—7—(9—10—11)—8

Atoms in direct combination are represented by 1—2. The degree of attraction decreases as we pass down in the series.

If we imagine, for example, that one of the positive hydrogen atoms in CH_4 has been replaced by C it follows that the methane carbon atom, $\overset{1}{C}$, will be essentially more negative in $CH_3—\underset{1}{\overset{2}{C}}$ than it was in methane. If, however, three hydrogen atoms are in union with $\overset{2}{C}$, it follows that $\overset{1}{C}$ will be less negative than it was originally in the methane. The truth of these deductions is obvious from a consideration of the chemistry of $\overset{1}{C}H_3 \cdot \overset{2}{C}H_3$, and may be accounted for by supposing that the sum of the positive influences of $\underset{3}{H_3}$ is greater than the single negative influence of $\overset{2}{C}$. "While the positions 2 and 3 are of the greatest importance, position 4 is subordinate and plays an even less important rôle than positions 5 and 6. The reasons for this are to be found in the fact that the indirect influences of 4 are less than 3 and much less than 2. The indirect influence of position 4 is so insignificant that usually it may be regarded as equivalent to 5—6—7—8. The direct attraction between atoms, which depends upon the relative distance of the atoms in space, obviously plays a much more important rôle than the indirect attraction in the case of positions 4—5—6, etc., and from this it follows that the sum of the influences for position 5, or for position 6, is greater

[1] Jour. Am. Chem. Soc., **32**, 999 (1910).

than for position 4 with respect to position 1." The relative influence of positions 9, 10 and 11 is uncertain and in general it may be said that the scale represents only the present state of our knowledge.

Formic acid, $\overset{1}{H}O\overset{2}{C}\overset{3}{\underset{\underset{O}{\|}}{H}}$, is by far the strongest acid of the series of acids represented by the general formula $C_nH_{2n+1}\cdot COOH$. If the hydrogen atom in position 4 is replaced by a methyl group, acetic acid is formed, $\overset{1}{H}O\overset{2}{C}\overset{3}{\underset{\underset{O}{\|}}{C}}\overset{4}{H}\overset{5}{_3}$, and in this new compound one carbon atom is to be found in the subordinate position 4, and three hydrogen atoms in the relatively more influential position 5. The derived acid, therefore, should be noticeably weaker than the original, and this reasoning is in harmony with the facts, the affinity constant, K, of acetic acid being roughly one-twelfth that of formic acid. Such disparity in the strength of the acids following each other in this series does not occur again, since in the derivation of propionic acid from acetic, for example, a negative carbon atom replaces hydrogen in the relatively important position 5, while the three new hydrogen atoms are added in the relatively less important position 6. For other illustrations see Jour. prakt. Chemie, 60, 333 (1899).

Recently these ideas of Michael have been partially verified and put upon a quantitative basis by C. G. Derick.[1] Derick holds that the best quantitative measure of chemical polarity is to be found in the free energy of ionization which is expressed in the affinity constant, K, (ionization constant) for acids and bases. He has demonstrated experimentally that the free energy of ionization in the case of all negatively substituted acids of the fatty series, in aqueous solution and at 25°, may be compounded additively from the individual effect of every atom in the molecule. It follows that the structural position of a negative substituent in a fatty acid molecule may be determined with certainty if the influence of the substituent in question is known.

For reasons, which are to be found in the original papers on the subject, the measure of the scale of influence of a given substituent upon a given ionizable group may be expressed thus:

$$\text{Place factor} = \frac{\text{log. K (of the unsubstituted acid)}}{\text{log. K (of the same acid after substitution)}} - 1$$

If, for example, the influence of the chlorine atom upon the carboxyl group in α-chlorbutyric acid is to be determined accurately, we must

[1] Jour. Am. Chem. Soc., **33**, 1152, 1162, 1167, 1181 (1911); **34**, 74 (1912).

also take into consideration the influence of the other atoms joined to carbon. The influence of the atoms in the radical

$$CH_3 \cdot CH_2 \cdot \underset{|}{CH} \cdot COOH$$

upon the ionization of the COOH must be the same as in the unsubstituted butyric acid if the influence of a single hydrogen atom be disregarded. In the case of butyric acid the value of K has been determined and $K = 1.56 \times 10^{-5}$, log. $K = -4.807$; in the case of α-chlorbutyric acid

$$K = 1.39 \times 10^{-3} \text{ log. } K = -2.857$$

and from this it follows that the place factor $= \frac{-4.807}{-2.857} - 1 = 0.6826$. Similarly the influence of all substituting groups may be expressed numerically provided that the ionization constants of the acids and bases in which substitution takes place are known. Thus, the place factors of the combined and indirect influences of chlorine on COOH in α, β, γ, and λ-chlorbutyric acids have been determined and found to to be respectively 0.6825, 0.1873, 0.0627, 0.0229. If the factor for the α-position is made equal to unity, the relation

$$1 : \tfrac{1}{3} : \tfrac{1}{9} : \tfrac{1}{27}$$

is established. That is to say, the effect of substituting a chlorine atom in the β-position is only $\frac{1}{3}$ that of substitution in the α-position, while the effect of substitution in the γ and λ positions is $\frac{1}{9}$ and $\frac{1}{27}$ respectively. The same rule has been found to hold for Br, I, OH and C_6H_5.

A great many phenomena in organic chemistry may be interpreted in terms of the principle of neutralization if the same laws which govern the neutralization of acids by bases be applied to processes taking place as the result of an exchange of atomic affinities. "Just as the weakest acid will combine with a small quantity of a given base even though the amount of base be infinitesimal as compared with the total quantity which would be necessary to neutralize completely all of the acid, so also will the weakest atom of a molecule compete with the strongest in an interchange of chemical affinities provided only that the transformation involves the formation of a new substance which is capable of existing, or a spontaneous dissociation involving an increase in the total entropy."

The more closely the two atoms of a double molecule resemble each other in their chemical affinity for a third atom, with which they both

can enter into combination, the more nearly equal will be the relative number of molecules of the two compounds which theoretically can be formed.[1] For example, let us assume that in a given reaction the atoms A and B of a molecule AB possess unequal attractions for the atoms C and D of the molecule CD. If now A has a greater affinity than B for C, a reaction of this order will take place provided that the affinities represented by the expression BD are greater than those of CD. The ease and completeness of the reaction will increase in proportion as the former value exceeds the latter. In addition reactions, however, other forces have to be taken into consideration. The course of the above reaction will be affected not only by the affinity of A for C and of B for D, but also by those of A for D and of B for C, and thus the possibility arises that combinations may take place not only in the sense $AC—BD$, but also in the sense $AD—BC$. In other words the latter reaction will be favored in direct proportion as the value $AC+BD>AD+BC$ becomes less. If now, these relationships are altered in such a way that the attraction of A for C becomes relatively greater than B for C, it follows $AC—BD$ will be formed at the expense of $AD—BC$, while if B has a greater affinity than A for D it may happen that the quantity of $AD—BC$ formed may be relatively so small as to be negligible.[2]

Inorganic chemistry deals with the mutual action of two electrolytes while organic chemistry treats with only one electrolyte. Whether the difference existing between these two branches of chemistry is to be found here or not is questionable. It is undoubtedly true, however, in organic reactions involving, for example, the affinities of A and B for C and D, that the formation of $AC—BD$ will take place if A has a more pronounced attraction for C than B has for D. The same change is also favored when A and B are not changed but CD is so altered that C, the more energetic of the two constituents, becomes relatively more reactive than B toward A.[3] Michael calls the relation which is derived in this way from the law of neutralization, the "distribution principle." It affords an explanation for the facts so frequently observed that rearrangements proceed at times with the formation of a single derivative and at other times with the formation of several.

Reactions involving molecular addition [4] and polymerization [5] may be readily interpreted from the standpoint of the principle of distribu-

[1] Jour. prakt., Chemie, **60**, 324 (1899).
[2] Jour. prakt. Chemie, **60**, 339 (1899).
[3] Jour. prakt. Chemie, **60**, 341 (1899).
[4] Jour. prakt. Chemie, **60**, 341 (1899); Ber., **39**, 2140 (1906).
[5] Jour. prakt. Chemie, **60**, 437, 443 (1899).

tion, but the relations become very involved when processes of substitution and cleavage are taken into consideration. In the case of the latter two different forces must be considered, namely, the energy which is needed to separate the atoms which constitute the organic molecule, and the relative attraction which the particular reagent has for the atoms in question. Such changes may, however, be interpreted in terms of the distribution principle if the following statement of Michael is valid: " the substitution of a hydrogen atom, attached to carbon, by an organic radical results in a relative increase in the positive or negative energy of the other atoms in the molecule. Whether the effect which is produced will be positive or negative in character depends upon whether the substituting group is relatively positive or negative as compared with hydrogen. If the effect is positive, it follows that the attraction of the carbon atom for such atoms as are relatively negative to carbon is increased, but that at the same time it is decreased to a corresponding degree for the relatively positive atom of hydrogen. The substitution of a negative radical decreases the power of the carbon to hold other atoms in the molecule." [1]

A. Michael and H. Leupold [2] have recently studied the course of intramolecular rearrangements in the case of alkyl bromides, and have brought forward experimental evidence which is of value in solving the problem as to the causes which operate to bring about a condition of equilibrium in reversible reactions. The rearrangements of propyl bromide, butyl bromide, etc., were investigated and it was found that both isobutyl bromide and tertiary butyl bromide rearrange, albeit at different rates, according to the following expression:

$$(CH_3)_2CH \cdot CH_2Br \rightleftarrows (CH_3)_3CBr$$

The reaction proceeds far more readily in the direction of the formation of the tertiary bromide than in the reverse direction. For example fifteen hours heating of the isobutyl bromide at 140° results in the transformation of about 74 per cent of the halide into the tertiary bromide. At this temperature the tertiary bromide shows no tendency to isomerize into the secondary bromide. When heated at a temperature of 184° for two or three hours isobutyl bromide is also converted into the tertiary compound to the extent of 74 per cent while the tertiary bromide yields a mixture containing 1 to 2 per cent of the secondary compound when heated at the same temperature for the same length of time. Again at 262° the secondary bromide undergoes

[1] Jour. prakt. Chemie, **75**, 105 (1907).
[2] Annalen der Chemie, **379**, 263 (1911).

rearrangement giving a mixture containing 74 per cent of the tertiary modification. In other words, this percentage of tertiary bromide represents a condition of equilibrium, and the slowness with which the reverse rearrangement takes place is due to the fact that the tertiary compound possesses relatively less free chemical energy than the secondary bromide. A primary decomposition in the sense of a dissociation apparently does not take place to any appreciable extent at the temperature of rearrangement. It is, therefore, impossible to explain the rearrangement by assuming that hydrogen bromide is first split off and then adds in a different sense so as to give an isomeric product.

The transformations in the case of the propyl bromides are analogous although not quite so easily studied. Michael and Leupold have explained the rearrangements of these substances from the standpoint of the law of entropy as follows: if hydrogen bromide adds to propylene the reaction must proceed in such a way that the maximum entropy possible under given conditions is obtained, with the result that the free chemical energy of the reacting molecules is changed as completely as possible into bound chemical energy. Molecular resistance to chemical change must, however, first be overcome in order that the reaction may proceed. In other words, a certain amount of energy must be expended in order to sever or at least to weaken the atomic unions or forces already existing, as, for example, between hydrogen and bromine, and represented by the bound chemical energy of the hydrogen bromide molecule. Since in the case of propylene addition the resistance to be overcome is the same whatever product is formed, it follows that addition in this case must necessarily result in the production of that one of all possible isomers which possesses the greater heat of formation. The molecular distribution of all opposing chemical forces is relatively more uniform in the isopropyl bromide molecule than in normal propyl bromide. The former substance has, therefore, a distinctly greater heat of formation than the latter [1] and, in fact, is practically the sole product of the addition of hydrobromic acid to propylene.

It has been observed very generally that the attraction of elements or compounds for each other increases with rise of temperature up to a given point and that from this point on it decreases until a second point is reached at which no combination takes place or at which, in other words, the compounds formed in the reaction are completely dissociated. The behavior of propylene toward hydrobromic acid may be considered in illustration. These substances unite at relatively low temperatures and their reactivity is increased with increase in temper-

[1] Jour. prakt. Chemie, **68**, 499 (1903); **79**, 418 (1909); Ber., **39**, 2140 (1906).

ature until finally a temperature is reached at which isopropyl bromide begins to dissociate. From this temperature on the tendency to addition becomes less until finally a point is reached at which propylene and hydrobromic acid no longer combine. Normal propyl bromide shows a similar tendency to dissociate at high temperatures. Since the secondary bromide represents a molecular arrangement of maximum entropy, the primary compound should show a tendency to pass over into this form. The reason why this rearrangement does not take place under ordinary conditions is due to the fact that the bound chemical energy in the molecule of normal propyl bromide is greater than the free chemical energy striving to bring about a rearrangement of the molecule. This bound energy can be conceived as operating between hydrogen and bromine on the one hand and between the other atoms of the molecule on the other hand. Upon heating, normal propyl bromide absorbs energy until finally at a given temperature there is a simultaneous loosening of hydrogen and bromine atoms from the rest of the molecule, and when sufficient energy has been absorbed to overcome the total chemical resistance to this change a rearrangement of the primary into the secondary bromide will take place. In the case of isopropyl bromide, which possesses much less free chemical energy than the normal bromide, isomerization takes place much less readily or, in other words, a greater amount of energy is necessary in order to overcome the resistance. It is to be noted, further, that isopropyl bromide has a greater specific heat than the normal bromide and is thus better able to absorb energy. From this it follows that the energy relations between the two isomers must necessarily change with rise in temperature and that while at ordinary temperatures the difference between the relative energies of the two substances is great, at high temperatures this difference becomes less. A similar relationship exists between the *iso-* and tertiary butyl bromides and accounts for the fact that the *iso*-bromide does not isomerize completely at high temperatures but gives a mixture consisting of 74 per cent of the tertiary and 26 per cent of the secondary bromide. This constant mixture represents apparently the maximum of entropy at high temperatures.

The rearrangement of isobutyl into tertiary butyl bromide is reversible. Now it is usually assumed that as a condition of chemical equilibrium is approached, the relative quantities of the substances formed during any instant bear the same relation as the relative velocities of the opposing reactions. A condition of equilibrium is reached when the velocities in opposite directions become equal. In other words such equilibrium is considered dynamic in that rearrangements take place in both senses although their resultant is equal to zero. The cor-

rectness of this conception has been put to experimental proof in the case of butyl bromide by Michael and Leupold. They determined the rates for both rearrangements and obtained results which were in direct contradiction to this fundamental law. This led Michael to the conclusion:[1] "in the experiments with butyl bromides the question as to the cause of the resulting condition of equilibrium in reversible reactions has been investigated experimentally for the first time and as a result it may be said that in this case the general assumption that such a process may be represented as dynamic in character has been found to be untenable. Equilibrium is here conditioned not by the velocity constant but by the more presence of the two bromides in the proportion of 74 per cent tertiary to 26 per cent secondary. This mixture probably represents the maximum of entropy possible under the conditions and when attained all further change ceases. In other words, the equilibrium is apparently static in character. It is, of course, possible to conceive a condition of equilibrium of this sort as static merely with reference to chemical reactivity in one direction or the other and at the same time to regard it as dynamic with reference to the energy relations, in that it may be assumed that a constant interchange of energy takes place between the two isomeric bromides."[2]

Michael distinctly avoids explanations of chemical processes which involve the use of mechanical representations. How he is able to maintain this attitude in dealing with the problems of stereochemistry may be learned by reading his treatise, "Die van't Hoff-Wisclicenussche Konfigurationslehre."[3] His theories conceive the problems of organic chemistry from a large point of view and it is possible by means of them to follow the course of organic rearrangements in much greater detail than ever before. Real progress is to be anticipated in the development of Michael's conceptions and it is to be expected confidently that not only will the quantitative applications of his theories be perfected but that their use will also be simplified.

[1] Annalen der Chemie, **379**, 285 (1911).

[2] For a further review of Michael's views the reader is referred to the following papers: Das Chinon vom Standpunkt des Entropiegesetzes und der Partialvalenzhypothese, Jour. prakt. Chemie, **79**, 418 (1909); Über Desmotropie und Merotropie Annalen der Chemie, **363**, 20, 36, 64, 94 (1908); Ber., **41**, 1080 (1908); Annalen der Chemie, **364**, 64, 129 (1909).

[3] Jour. prakt. Chemie, **75**, 105 (1907); Am. Chem. Jour., **39**, 1 (1908); Ber., **41**, 2907 (1908); Ber., **42**, 310, 317, 3157 (1909).

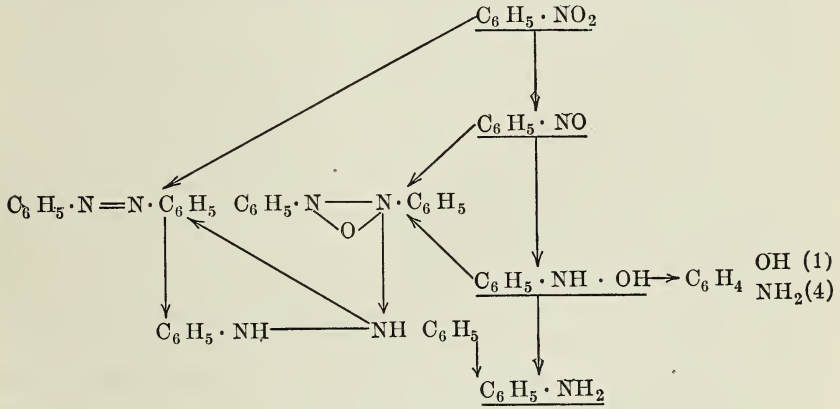
CHAPTER XXII

RECENT ELECTROCHEMICAL THEORIES

The mechanism of the process of reduction in organic chemistry was first investigated systematically in connection with a study of the nitro-derivatives of the aromatic hydrocarbons. Thus W. Löb,[1] taking as a basis the pioneer work of K. Elbs,[2] Häussermann,[3] and Gattermann,[4] interpreted the mechanism of the reduction of nitro-compounds in alkaline solution by supposing that the first step in such a process is the formation of intermediate *ortho*-hydrate combinations:

$$C_6H_5NO_2 \rightarrow C_6H_5N(OH)_4$$

It was assumed that in the course of alkaline reduction the radicals $RN(OH)_3—$, $RN(OH)_2=$, $RN(OH)\equiv$, $R\cdot N\equiv$, were successively formed, and that azoxy-, azo-, and other reduction products were produced as a result of the subsequent coupling of these radicals. In 1898, however,



F. Haber[5] was able to demonstrate that nitrosobenzene and phenylhydroxylamine were formed in both alkaline and acid solution as primary reduction products of nitrobenzene, and that in alkaline solutions they combine to give azoxy-compounds. In strongly acid solutions C_6H_5NHOH rearranges to give *p*-amidophenol, and in the presence of weak acids it is reduced to aniline. The so-called " Haber scheme of reduction " has been developed as a result of this investigation:

[1] Zeitschr. Elektrochemie, **2**, 529 (1896); **3**, 471 (1897).
[2] Jour. prakt. Chemie, **43**, 39 (1891).
[3] Chem. Zeitung. (1893), 129, 209.
[4] Ber., **26**, 1844 (1893); **27**, 1927 (1894).
[5] Zeitschr. Elektrochemie, **4**, 506 (1898).

In this scheme the directly descending arrows on the right represent the process of electrolytic reduction, while all others represent purely chemical transformations and rearrangements.[1]

Recent developments in the field of electro-chemistry and related subjects might be expected to throw new light upon the atomic relations of matter. It is, therefore, necessary to pause for a brief historical review of this subject in order to ascertain whether the new interpretations which were evolved in this way really escape the charge of one-sidedness, which the application of Kekulé's structural theories brought with them.

The fundamental defect in the theories of Berzelius was that they failed to establish any numerical relationship between electrical attraction and chemical affinity. The first fundamental law governing such a relationship was discovered by Faraday in 1833, and may be stated as follows: "the amount of substance which is decomposed, as the result of the passage of the electric current, is proportional to the quantity of current, and the amounts of different materials formed by decomposition in a given interval of time, bear the same relation to each other numerically as their respective chemical equivalents." This law of Faraday's introduced the quantitative period of electrochemistry.

Faraday's law exercised no influence upon the theories of Berzelius, and was indeed in such apparent contradication to the fundamental assumptions upon which these theories were based that the great Swedish chemist even doubted Faraday's results. Berzelius had assumed that different atoms possess different charges of electricity, and that the greater the positive and negative charges of two reacting atoms the stronger will be their attraction for each other. Faraday's investigations proved conclusively that all atoms possess equally great positive and negative charges, but failed to answer the question as to what constituted the difference in chemical attraction between different atoms.

Faraday had distinguished quite definitely between the strength of current and the intensity of the current (electromotive force), but Berzelius used the two terms interchangeably, and therefore assumed that equal quantities of electricity must also represent an equal degree of chemical attraction. It thus happened that Faraday's law was not embodied in the leading theory of his day, and remained comparatively

[1] K. Elbs, "Übungsbeispiele für die elektrolytische Darstellung chemischer Präparate," 2. Aufl., Halle, 1911; K. Brand, "Die elektrochemische Reduktion organischer Nitrokörper," Stuttgart, Enke, 1908; Loeb, "Elektrochemie organischer Verbindungen"; A. Moser, "Die elektrolytische Prozesse der organischer Chemie," Halle, Knapp, 1910.

unnoticed until 1881, when H. von Helmholtz incorporated it in the valence theory, which had in the meantime come into prominence.

The electrochemical terms in common use at the present time such as, for example, electrode, electrolyte, cation, and anion, etc., owe their origin to Faraday. Substances whose movements were directed towards the two electrodes were called ions, and the study of these ions brought about step by step the most important developments in the theory of electrochemistry. It took decades to complete the chain of these developments but this was partly Faraday's fault since hindrances as well as guides to further important investigations are to be met with side by side in his work. For example, he had observed that weak currents may pass through electrolytes without effecting any apparent decomposition and he, therefore, assumed that this was due to the existence of a second type of electrolytic conductivity which resembled the conductivity of the metals. Only the later investigations of Buff and others served to dissipate these ideas and to establish the fact that the passage of an electric current through solutions is always accompanied by chemical decomposition. It has been calculated that the quantity of electricity necessary to decompose one gram equivalent of any substance is equal to 96540 coulombs. Since the equivalent weight of an element is equal to its atomic weight divided by its valency, Helmholtz was able, in 1881, to point out the relationship existing between Faraday's law and the theory of valency. In his famous "Faraday Lectures" Helmholtz gave the following expression to the *law of electrolysis* as applied to solid bodies: "the same quantity of current in equal periods of time sets free an equal number of valencies in different electrolytes, and causes them to assume other forms of combination." The fact that not only acids, bases, and salts, but that all substances may be regarded as electrolytes led Helmholtz to the further development of this conception which he expressed as follows: "if every unit of affinity is charged with an equivalent amount of electricity, whether positive or negative, it follows that the electrically neutral bodies must arise as a result of the mutual combination under the influence of the powerful electrical attraction of units which are respectively positively and negatively charged. It is obvious that in the compounds which arise in this way, every unit of affinity possessed by an atom must be in union with one and only one other unit of affinity possessed by another atom. This must be recognized at once as the modern theory of valency and includes all saturated compounds." "Unsaturated compounds which possess an even number of free units of affinity furnish no ground for objection to this hypothesis, since they

may be imagined as charged with equal amounts of positive and negative electricity."

If Faraday delayed progress in the development of electrochemical theory by his false assumption that electrolytes were capable of metallic as well as of electrolytic conduction of electricity, he certainly gave the impulse for extremely important discoveries in the field of affinity relationships by a remark in one of his later papers. In 1840 he pointed out that the electric current can do work. Now if electrical energy could result, by mere contact, it would follow that energy (work) could be created out of nothing. This idea, soon after the discovery of the law of conservation of energy led W. Thomson and Helmholtz to apply systematically the law of the mechanical theory of heat to the phenomena of electrolysis.

When a compound is decomposed by the electric current, the work done must be sufficient to overcome the sum of all the forces which hold together the various parts of the molecule. This would be represented by the product of (*a*) the quantity of electricity necessary for decomposition, and (*b*) the electromotive force. Since, moreover, the same quantity of electricity (96540 coulombs) is necessary for the decomposition of each gram equivalent, irrespective of the kind of matter, it follows that the work is, therefore, proportional to the electromotive force. Since the work necessary to decompose a given chemical compound must, moreover, be the same as that necessary for its formation, the electromotive force may be regarded as the measure of chemical affinity. It is not possible to discuss fully at this time how these facts led to the discovery that actually only a relatively small fraction of the total affinity, which Helmholtz called the free energy of the atoms, is proportional to the heat of formation of a given molecule, but it is obvious that affinities can be measured in the case of reversible processes by the determination of the electromotive forces. Calculations by Helmholtz, Richarz, and Ebert show that the electrical forces which hold the atoms together are of such magnitude that they must be the principal if not the only forces which are at work in the molecule.

The so-called ionic theory, which has played such an important part in the development of inorganic and analytical chemistry, offers a very probable explanation for the phenomena which have just been described. Energy conceptions have led to the assumption that in solutions which conduct electricity the molecules are already dissociated into ions, so that this work does not need to be done by the electric current. In the sense of this theory the ions may be either single atoms or atomic complexes charged with one or more units of positive or negative electricity. They are entirely different from the elements

in their properties and are regarded by Nernst as saturated chemical compounds. The different ions are to be distinguished from one another by the fact that they are able to bind their electrons more or less securely, or, in other words to hold their electric charges more or less firmly. Nernst succeeded in finding in the so-called dissociation tension a definite measure for the energy which binds an electron to a given atom or group of atoms to form an ion and he was able to do this by a very ingenious combination of the laws of osmosis and the ionic theory. It has been observed that a definite amount of electromotive power is necessary for the electrical discharge of an ion, and that this value is constant for ions of the same kind but is different for different ions. In this way it is possible to obtain numbers which express the relative strengths of union of a unit of electricity with the different atoms and groups of atoms.

A system which is based upon the electron theory has been developed by R. Abegg and G. Bodländer. This has been of the greatest value in systematizing inorganic compounds but since it is also applicable to organic compounds, it may be briefly outlined at this point. These investigators consider the relation of the atom to the unit charge, i.e., the electron, rather than the relation of one atom to another atom. This value, which is measurable, is called the electro-affinity and is regarded as inherent in the atoms. It is, however, capable of holding only a limited and relatively small number of other atoms no matter how great the strength of affinity of any particular atom. A new conception of valency was based upon these considerations. If atomic and molecular compounds are to be interpreted from a common point of view it is not possible to assume a constant valency for the atoms, but a maximum valency which is not always fully attained in all the compounds of the elements. The number of valencies which a given atom may exercise will vary according to the nature of the element combining with it. This variation of valency takes place in a regular manner. Thus the greater the difference between one element and another, the greater will be the valency shown by one for the other. A measure of the difference between elements is to be found in their electro-affinity, and this may be readily estimated and tabulated according to the periodic classification, the greatest extremes of electro-affinity being found in elements at the ends of the horizontal series.

Electro-valence is the name given by Abegg to that valence which is exercised in holding the ionic charge, and he seeks to reduce the expression of all affinity to the mutual action of electro-valencies. He further assumes that all elements possess positive as well as negative maximum valencies, and that in every case the sum of these is eight.

The electro-valency of the element is therefore polar in character. *Normal valencies* is the name given to those positive or negative valencies which while fewer in number are stronger in effect, while *contra-valencies* is the name given to the other type of valencies. Thus the positive maximum valencies of an atom correspond in number to the group number of a given element in the periodic system, as will be seen by reference to the following table:

I	II	III	IV	V	VI	VII	Groups of the Periodic System
+1	+2	+3	+4	−3	−2	−1	Normal-valencies
−7	−6	−5	−4	+5	+6	+7	Contra-valencies

The old idea of Berzelius is thus resurrected, clothed in modern phraseology, and given a more definite quantitative expression.[1]

In the groups represented at the extreme right and left of the table the polar character of the element is strongly marked, and is decidedly positive or negative, since the value of the normal valence is in each case equal to 1. Near the middle of a horizontal series the normal and contra-valencies become more nearly equal in number and strength. Because of this the atoms become less pronounced (i.e, decidedly positive or negative) in their chemical affinities. The carbon atom is especially conspicuous as belonging to a group where the normal and contra-valencies are equal in number. According to Abegg this accounts for the ability of carbon to combine not only with other carbon atoms but with both positive H, Zn, etc.), and negative (Cl, O, etc.) elements. Thus it happens that the methyl group may function as a negative group as in $Zn(CH_3)_2$, and as a positive group, as in (CH_3Cl).

In order to answer the question as to why only four valencies of the possible eight are commonly exercised by carbon, Abegg assumes that the exercise of one kind of valence prevents the functioning of the other. Thus if a positive electro-valence is saturated, the corresponding negative valence becomes inactive. If the mutual union between carbon atoms depends upon their opposite polarity it follows that in $CH_3 \cdot CH_3$ the two carbon atoms have different functions. It has been noted that in other compounds CH_3 may function as a positive or as negative group, so that this idea need not seem impossible when applied to ethane.

In C_2H_5Cl the carbon atom exercises a positive valence for the chlorine. It might be supposed that, as a result of this, it would be more inclined to develop a negative valence for the carbon atom adjacent

[1] D. Mendelejeff, " Grundlagen der Chemie," 5th Edition, 1889, p. 304.

to it. Experience shows that further chlorination results in the substitution of a second chlorine atom on the carbon which already holds one, and it may be supposed that the exercise of a second positive valency strengthens the original inclination of this carbon atom to exhibit a negative valency for the carbon of the adjacent CH_3 group. It may even be that this propensity on the part of two carbon atoms to combine mutually by means of polar valencies accounts for the tendency of chlorine to combine with carbon already holding chlorine (thus increasing the polarity of the carbon), and also for the following rearrangements and additions:

$$CH_3 \cdot CH_2 \cdot CH_2Br \rightarrow CH_3 \cdot CHBr \cdot CH_3$$

$$CH_3CH{=}CH_2 + HI \rightarrow CH_3CHI \cdot CH_3$$

It may also account for the ease with which CO_2 is split off from acids of the formulas $>C(COOH)_2$ and NO_2CH_2COOH and, further, for the fact that in aromatic compounds the substitution of a negative group takes place in the *meta-* rather than in the *ortho*-position with reference to a negative group already substituting in the ring. By this arrangement it is obviously possible for the two carbon atoms bearing negative groups to exercise negative polar valencies for the carbon atom which occupies an intermediate position between them.

Although the CH_3 group may exercise a positive or a negative valence, facts go to show that its preference is for the former. The CH_2 group, in which only two negative valence-electrons of carbon are exercised in holding hydrogen, reacts negatively toward other atoms more readily than the methyl group and, in general, the less hydrogen there is in union with carbon the greater the ease with which the latter will function negatively toward other atoms. The negative character of unsaturated radicals tends to confirm this view.

Abegg gives the following interpretation to the constitution of organo-ammonium salts. In terms of the present theory it must be assumed that the nitrogen atom in NH_4Cl exercises more than one kind of valency. Since only three of the positive hydrogen atoms can unite with the three negative valencies of nitrogen (*three* being the maximum number of normal valencies for this element) the fourth hydrogen atom is called upon to exercise its own negative contra-valence toward a positive contra-valence of nitrogen. The instability of this union is clearly shown by the ease with which ammonia is split off from ammonium salts and is evidence of the weak affinity of positive nitrogen valencies. If alkyl groups replace the hydrogen in an ammo-

nium salt, it follows that nitrogen valencies are now exercised toward carbon. That the negative valencies of carbon are much stronger than those of hydrogen is shown by the existence of alkyl metallic hydroxides while the corresponding compounds with hydrogen do not exist. Thus of the four substituting groups three combine with negative valencies of nitrogen, while the fourth combines perforce with a positive nitrogen valence. And it is here that a striking increase in the stability of the molecule is to be observed. The instability of substituted ammonium salts containing less than four alkyl groups may be assumed to be due to the dissociation of the N′—H′ union, and from this it follows that the first three alkyl groups must combine with nitrogen by means of its three negative valencies, for if any one of them had combined with a positive valence of nitrogen the union would be stable.

There can be no doubt but that the introduction of elements and radicals of marked polarity (metals, oxygen, halogen, etc.) into organic compounds increases enormously the chemical reactivity of these substances. This may be explained by supposing that the particular atom, or group of atoms, gives chemically neutral or indifferent compounds when in union with polar partners which are not essentially different from it (as, for example, C and H) and that, on the other hand, it becomes chemically active in the presence of substituting groups of marked polarity, through the necessity of developing an opposite polarity for itself. For example, $CH_3 \cdot H$ does not react with HCl because CH_3 and H are so much alike that neither develops polarity in the other while, on the other hand, $CH_3 \cdot OH$ does react with HCl because the radical CH_3 is forced into playing a definitely positive rôle through the presence of the negative OH group. In the latter case CH_3Cl and H_2O are formed as a result of the double decomposition of the two molecules. CH_3 reacts with HCl in quite a different sense when playing a definitely negative rôle as in $(CH_3)_2Zn$. In this case CH_3H is formed along with CH_3Cl as a result of the reaction with HCl. That the same group reacts differently with a given reagent under different circumstances, is important only in so far as it shows that reactivity goes hand in hand with a marked difference in polarity of the parts within a molecule.

Abegg [1] has recently given particular attention to the interpretation of those chemical changes which are included under the head of the Grignard reactions and which involve combinations of magnesium alkyl halides with aldehydes, ketones, esters, and other unsaturated molecules. It has been noted that alkyl radicals may function in either a positive or negative capacity. In alkyl magnesium halides the

[1] Ber., **38**, 4112 (1905).

alkyl group must be imagined as compelled to play a negative rôle for which it has no liking. Thus there is a tendency in the molecule for the alkyl to abandon this rôle for one more to its general satisfaction, and, simultaneously, a tendency for the magnesium halide complex to seek for itself a more comfortable companion. These two tendencies represent the impelling forces at work in magnesium halogen compounds. They are neutralized during the process of addition to ketones since the influence of doubly bound oxygen asserts itself and affords the magnesium halogen residue an opportunity to enter into combination with the stronger of the two negative valencies of the oxygen, while at the same time the alkyl radical attaches itself to the free valency of carbon. That this carbon valence functions in a positive sense is obvious from the fact of its previous union with a negative oxygen atom. It is equally obvious that the new adjustment of valencies makes for a more stable condition in the molecule.

The reaction of organo-magnesium halides with acid esters leads to interesting deductions in regard to the polar character of the components of the esters. These bodies react in either of two ways depending upon the reagent employed:

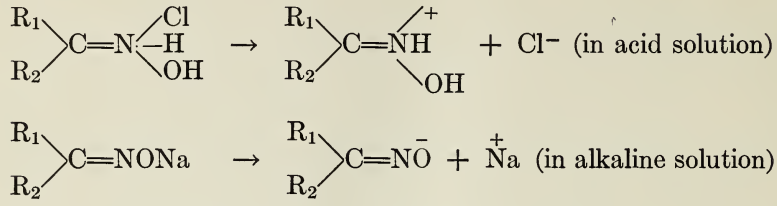
$$(R\cdot COO)^- \text{ Alkyl}^+ \qquad \text{or} \qquad (RCO)^+ (O\text{—Alkyl})^-$$

With a Grignard reagent the reaction takes place in the latter sense and the magnesium halogen residue combines with (—O Alkyl). A second molecule of the alkyl magnesium halide then reacts with a carbonyl group and at the same time the alkyl group of the first molecule of halide combines with the carbon to give $(\text{Alkyl}_3\text{—C}\cdot O)^-\cdot (\text{Mg}\cdot\text{Halogen})^+$. The addition of CO_2, COS, and SO_2 to the organic part of the organo-magnesium compounds bears evidence to the need of such radicals to become better fitted for the negative function forced upon them by the magnesium.

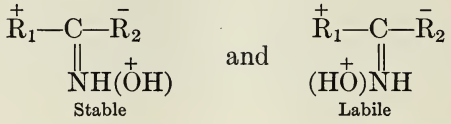
Abegg also discussed, from the standpoint of the present theory, the conditions governing the relative stability and the rearrangements of the stereoisomeric oximes, the discussion being essentially the same as that given in an earlier paper.[1] Oximes frequently give salts with acids as well as with bases. If these salts are dissolved in water, the ion of the oxime sometimes functions as the cation (acid solution) and sometimes as an anion (alkaline solution) receiving thus in one case a positive, and in the other case, a negative charge. This is most readily interpreted by supposing that the charge is located in that part of the

[1] Ber., **32**, 291 (1899).

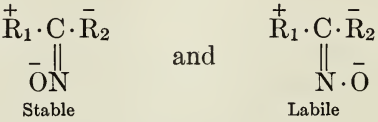
molecule from which the dissociation of the other ion takes place, viz., on the oxygen of the oxime group. For example:



It may be assumed, further, that R_1 and R_2 also possess charges of electricity and that those oximes would be most stable in which the arrangement of parts is such that the positively charged radical is placed immediately opposite the hydroxyl group of the oxime. Thus in acid solution the stable and labile forms are respectively:



and analogously in alkaline solution there would be present



This offers a basis for determining the relative stability of oximes, since the dissociation constants of acids and bases, which contain R_1 and R_2 in suitable forms of combination, make it possible to construct a table showing the relative influence of these respective radicals. According to Abegg, the series runs as follows:

$$-COOH,\ Cl,\ C_6H_5,\ C_6H_5X,\ H,\ Alkyl,\ CH_3$$

and agrees in all essentials with the series arranged by A. Hantzsch [1] to show the relative chemical attraction of radicals for the oxime group.

In conclusion it may be said that it is exceedingly difficult to formulate a composite picture of the theories of organic chemistry. The present treatise has, therefore, confined itself to a consideration of certain of the more fundamental conceptions which are of general application, and has endeavored to point out in each case the strength and the weakness of the individual views. In this way a certain unity in the

[1] Ber., **25**, 2164 (1892).

development of the theory of organic chemistry has, however, become apparent. Thus the earlier ideas in regard to unit valencies have been observed gradually to give place to more detailed and complex conceptions in regard to the existence and function of so-called partial valencies. The questions about which the greatest interest now centers have come to be those which involve the distribution of affinity among the different parts of the molecule under different conditions and which, therefore, require for their solution not merely the application of chemical methods but frequently of physical methods as well. Since it has often been difficult to harmonize the data which have been obtained from these different sources, a definite effort has been, and is still being made to bring about a more satisfactory correlation of physical and chemical methods, and it is to be hoped that the future will see material progress in this direction. It may be added that because at the present time a correct understanding of the constitution of organic compounds involves a knowledge of the constitution of the atoms themselves, future important developments in the field of organic chemistry must necessarily depend upon the ability of the chemist to interpret the data which may become available in the future as the result of the exact application of physical methods.

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